Adsorptive removal of Pb(II) ion from aqueous solution using rice husk-based activated carbon

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

(Mohd Faisal B. Taha)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(AHMAD SHAKEEL BIN ROSMAN

ACKNOWLEDGEMENT

In the name of ALLAH S.W.T, the most merciful and compassionate, praise to ALLAH, he is the Almighty, eternal blessing and peace upon the Glory of the Universe, our beloved Prophet Muhammad (S.A.W), and his family and companions.

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ABSTRACT

There are various methods can be used to remove heavy metals from waste water, such as chemical precipitation, ion exchange, electroplating and membrane separation. Nevertheless the most effective method would be adsorption using activated carbon due to its large number of pores. This project will be focusing primarily on rice husk as potential activated carbon as low cost adsorbent to remove Pb(II) from wastewater. Preparation of activated carbon involves three steps which are raw rice husk preparation, activation stage and carbonization stages. Preparation of rice husk involves grinding to 63 μm which is then treated with 1.0 M of sodium hydroxide (NaOH). The treated rice husk is then carbonized at 500°C for 2 hours to remove volatile organic components. After the activated carbons are produced, extraction study will be carried out to further study the adsorption capacity. The pores development of the rice husk was analysed using Field Emission Scanning Electron Microscope (FESEM). Other analyses for rice husk based activated carbon were conducted using TGA, XRD, CHN Elemental Analyser and FTIR for characterisation study on the particles of rice husk. Pb(II) ion extraction from aqueous solution was done using rice husk based activated carbon which was conducted at different contact time at room temperature. The adsorption capacity of Pb(II) ion was determined using Atomic Adsorption Spectroscopy (AAS). Results obtained from adsorption study indicate that rice has the potential to be used as adsorbent for heavy metals removal.

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CHAPTER 1: INTRODUCTION

1.1 Project Background

Nowadays, the contamination of heavy metal exists in waste water from various industries throughout the world such as metal plating, mining, tanneries, painting, car radiator manufacturing and that includes agricultural sources whereby fungicidal spray and fertilizer are frequently used. Some of the dangerous and harmful wastes include Pb, Zn, Cd, that pose risk of contaminating groundwater and other available water resources. Heavy metals are not easily biodegrable and they tend to accumulate in living organisms which leads to different types of diseases and disorders. Therefore, it is recommended to remove or reduce the amount of heavy metals concentrations to an acceptable level before released into the environment. (T.G Chuah et al., 2004)

There has been a variety of methods used to remove metal ions such as precipitation, adsorption, evaporation, reverse osmosis and ion exchange. Among them, adsorption with activated carbon is considered to be the best technology for the removal of heavy metals from waste water except for its high manufacturing cost. Recently, researches have been seeking for more cost-effective ways to obtain the carbon which can be produced from any types that are rich in carbon element. Some of those materials are rice husk, coconut shell, wheat straw and sawdust. These materials are utilized as the precursors of activated carbon to remove heavy metals (Jinghui Zhang et al., 2010). Adsorption is favourable for metal ions recovery purposes due to its simplicity, selectivity and efficiency. It is suitable to adsorb and separate low molecular weight compounds and free metals.(N.S Awwad et al., 2010). Rice husk is used for this project since it is available locally; cost effective and less expensive technology is required.

Activated carbons are the most popular adsorbents used for the removal of toxic substances from water. This is due to the fact that they have a high adsorption capacity, high adsorption rate and good resistance to abrasion. Increased use of activated carbon has made it necessitated the exploitation of readily available and low cost sources agricultural waste products. Activated carbon is a good adsorbent as it has extended

surface are, porous structure with micropores, mesopores and macropores (Rumi Chand et al., 2009). These macropores actually has no significance to the surface area of carbon, instead they provide passage to the micropores and particle interior. The micropores are developed primarily during carbon activation process and result in large surface area for adsorption to occur.

1.2 Problem Statement

Heavy metals are toxic because they are present as ions in an aqueous system and can be readily absorbed into the human body. Since heavy metals are not biodegrable, accumulation and distribution of these metals to the environment is a serious concern towards the public. Even a very small amount can cause severe physiological or neurological damage (K.K Wong et al., 2002). The rise of the contamination of water by toxic heavy metals through the discharge of industrial wastewater has become a worldwide environment problem that cannot be easily resolved. The table below displays the Environment Quality Act 1974, for the Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979 in Malaysia with selected limits of heavy metals effluent.

Table 1. Environment Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979: Selected limits of effluent for Standard A and B (Department of Environment, DOE, Malaysia)

Parameter, (mg/L)	Standard	
	A	B
Cadmium	0.01	0.02
Zinc	1.0	1.0
Copper	0.20	1.0
Nickel	0.2	1.0

Mercury	0.005	0.05

All lead compounds are highly toxic. Extreme lead poisoning may cause a variety of neurological disorders (Qingge Feng et al., 2004). Despite the elimination of lead from many consumer applications in recent years, due to health and environmental concerns, lead is still an important metal with many uses in several industries. Because of its abundance, low cost, and physical properties, lead and lead compounds have been used in a wide variety of products including paint, ceramics, pipes, solders, gasoline, batteries, and cosmetics. Most lead is added during industrial activities which can be found in wastewater from printed circuit board factories, electronics assembly plants and battery recycling plants.

1.3 Objective & Scope of Study

Below are the objectives of this study:

1) To study and analyse the capabilities of rice husk as an adsorbent to adsorb Pb(II) ion from aqueous solution.

2) To study the pores development of rice husk throughout the process.

3) To determine the adsorption capacity of rice husk activated carbon digested with sodium hydroxide (NaOH).

1.3.1 Relevancy of the Project

Activated carbon prepared from rice husk can be used as low cost alternative adsorbent to remove heavy metal ions from industrial wastewater. This is critical to ensure that the heavy metals are removed from wastewater so it can be safely used and avoiding any dangers to the environment. Nowadays, there are various existing methods that can be used to treat wastewater. However, each comes

with their own disadvantages and there's another issue of high implementation cost. For this study, rice husk as an agricultural waste, could be the answer for a cheaper alternative commercial activated carbon for the removal of Pb(II) ion by adsorption process.

1.3.2 Feasibility of the Project Within Scope and Time Frame.

The raw rice husks are readily available here in UTP. The rusk husk will need to be properly cleaned with distilled water to remove any impurities, blended to get smaller particle sizes and sieved to 63 μm size before begin treating with sodium hydroxide (NaOH). The rice husk will then undergo carbonization process to obtain activated carbon. There are a few adsorption studies that will be performed in order to find the activated carbon's adsorption capacity. There are quite a number of studies focusing on rice husk based activated carbon that can be used as reference. All equipment required for this project is available in Chemical Engineering Department Laboratory or from other department's laboratory that can be borrowed temporarily. This project can be finished in a year, now with all resources provided; this project can be considered as feasible project within the time frame given.

CHAPTER 2: LITERATURE REVIEW

2.1 Adsorption

Adsorption can be defined as process whereby activated carbon extracts metal ions from waste water. It is basically a process that removes certain particles which are bound to any adsorbent particle surface by physical or chemical attraction. It is widely used in the industry such as activated charcoal, water purification and synthetic resins. Sorption processes like adsorption, ion exchange and chromatography are selectively transferred from fluid phase to the surface of rigid particles in a vessel.

There are 2 types of adsorption depending on the forces involved, physical and chemical adsorption. For physical adsorption (physisorption), adsorbate is bound to the surface by a weak van der Walls forces. However for chemisorption, there is an exchange of electrons between the surface of adsorbent and the adsorbate molecules that leads into a chemical reaction. The bond formed between adsorbent and adsorbate is chemical bond that makes it stronger than physisorption (Roop Chand Bansal & Meenakshi Goyal, 2005).

2.2 Factors effecting adsorption

2.2.1 Particle size

The smaller the size of particles, then the higher the adsorption capacity gets as the surface are grows larger (Qingge Feng et al, 2004). It is expected that adsorption capacity will increase with larger surface area, this means that smaller sized particles also helps to increase adsorption capacity. The quantity of metals ion adsorbed decreases as the particles of rice husk increases (E. Munaf and R.Zein, 1997). Since adsorption itself is a surface phenomenon, larger adsorption sizes offers smaller surface areas and lower adsorption will happen at equilibrium.

2.2.2 pH level of activation agent

It's already known that sorption of heavy metals also depends on the pH level of the solution. It has also been suggested that contents of amino acid acids, the active functional groups and metal oxides in rice husk might affect the uptake process (Mishra et al. 1997). Surface of adsorbent is surrounded by hydrogen ions at low pH preventing metals from nearing binding sits on the sorbent (K.K Wong. Et al, 2003). This means that it also restricts the uptake of Pb(II) ions. The adsorption capacity increases with increasing pH values.

2.2.3 Carbonization time of rice husk

Adsorption might decrease as carbonization time increases that result in higher carbon burn off which decreases the porosity of adsorbent (R.M Suzuki et al, 2007). The reason for this is because of thermal destruction of pores structure as the carbonization time increases or even the blockage of pores entrance caused by the formation of ash (Shasanka Sekhar, 2009). Increased burning time will in turn maximize the amount of silica, however this also led to a significant reduce of the amount of carbon content. With the amount of carbon reduced, this will decrease the adsorbent's porosity.

2.2.4 Carbonization temperature of rice husk

Higher temperature leads to increase of metal ion adsorption (Jinghui Zhang et, al 2010). The purpose of carbonizing is mainly to eradicate any impurities besides carbon and provide a fixed carbon mass. Some of the factors that affect the quality of activated carbon are listed below:

a) Heating rate
b) Final temperature for heating.
c) Soaking time at the final temperature.
d) Enhanced mechanical strength.
e) Nature and physical state of the raw material available.

2.2.5 Contact time of adsorption activities

The longer the contact time is, and then the rate of ion adsorption would be higher, until the process reaches equilibrium (Guo et al., 2000). Fast kinetics between rice husk and Pb(II) ion depends entirely on the analytical speed and efficiency of removal. For that reason, this factor needs to be constant as the effect of contact time is tested over the course of the project.

2.3 Rice husk as low cost adsorbent

The abundance of rice husk available locally makes it an ideal source of inexpensive raw materials for natural adsorbents. Rice husk are usually burned in the field or discarded which is not favourable to the environment. If it is not utilized properly, this will result in huge waste generation and environmental pollution (Yue Chen et al., 2011). Rice husk has also been reported to be a good sorbent of many metals and basic dyes (T.G Chuah et al., 2004). Table below shows the maximum lead adsorption capacities for rice husk that have been previously reported by other researchers.

Table 2. Reported maximum lead adsorption capacities for rice husk

Roy et al., 1993	11.40
Wong et al., 2003	108 (27°C)
	105(50°C)
	96 (70°C)
	129.48 (single metal solution
	48.31 (bi-metal solution)
Tarley et al., 2004	21.55 (modified with NaOH solution)
	45 (unmodified)

It has also been discovered that treated rice has higher adsorption capacity as the porosity increases compared to natural rice husk (Cesar Ricardo Teixira Tarley, et al., 2004; Hengpeng Ye, et al., 2010). Based on the statistics compiled by the Malaysian Ministry of Agriculture, there are almost 408 000 metric tonnes of rice husk, a commodity crop residue, is produced in Malaysia with each passing year (K.K Wong et al., 2003). Therefore, by converting rice husk into activated carbon would eliminate the problems of disposal and waste management (Yue Chen et al., 2011).

Table 3. Reported physiochemical characteristics of rice husk

Bulk density (g/ml)	0.73
Solid density (g/ml)	1.5
Moisture Content (%)	6.62
Ash Content (%)	45.97
Particle size (mesh)	200-16
Surface areacidity (m2/g)	272.15
Surface area acidity (meq/gm)	0.1
Surface basicity (meq/gm)	0.45

Treated rice husk that are transformed to activated carbon is much more capable of functioning as adsorbent since there are pores development. The basic chemical components, composition and physicochemical characteristic are displayed in the table below:

Table 4. Composition of rice husk

Cellulose	32.34
Hemicellulose	21.34
Lignin	21.44
Mineral Ash	15.05

Table 5. Chemical composition in mineral ash

SiO	96.34
K_2O	2.31
MgO	0.45
Fe_2O_3	0.2
Al_2O_3	0.41
CaO	0.41

2.4 Activated Carbon

Activated carbon, also known as activated charcoal, activated coal or *carbo activatus*, is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions.

2.4.1 Properties of activated carbon

Due to its high degree of micro porosity, only 1 gram of activated carbon can a surface area in excess of $500m^2$, with $1500m^2$ readily available achievable. Sufficient activation for useful applications may come solely from the high surface area, with further chemical treatment may enhance the absorbing properties of the material. Properties of a good activated carbon are list below:

- High degree of surface reactivity
- Universal adsorption effect
- Large surface area
- High degree of surface reactivity
- Enhanced mechanical strength.
- Pore size as access route to internal surfaces.

Activated carbon is very useful in drinking water treatment because it can act as adsorbent that effectively remove and extract any organics and foreign particles from

water. Another factor that makes activated carbon an effective adsorbent is because it has many cavernous pores that provide large surface area to the size of actual carbon particle.

2.4.2 Porosity Of Activated Carbon

Pores in activated carbon are formed by a series of processes.

1) Removal of water (Dehydration)
2) Conversion of the organic matter to elemental carbon, driving off the non-carbon portion (Carbonization)
3) Burning of tars and pore enlargement (Activation)

Based on study conducted by K.S Low, C.K.Lee and S.C Liew, treatment with base such sodium hydroxide (NaOH) greatly enhanced metal sorption compared to using acid whereby HCl treated spent grain showed lower sorption than the control material (water-washed spent grain). Marshall and Jones reported that NaOH treated soybean and cottonseed hulls improved sorption capacity for Zn(II) as compared to the untreated materials. Other work has also shown that sodium hydroxide treated waste products have greater sorption capacity than unmodified materials. Activated carbon has also been prepared with KOH and NaOH and the result was that the treatment by using NaOH has shown to produce larger mesopore and pore diameter. Larger pore diameters have led to a larger adsorption capacity (Yupeng Guo et al., 2002).

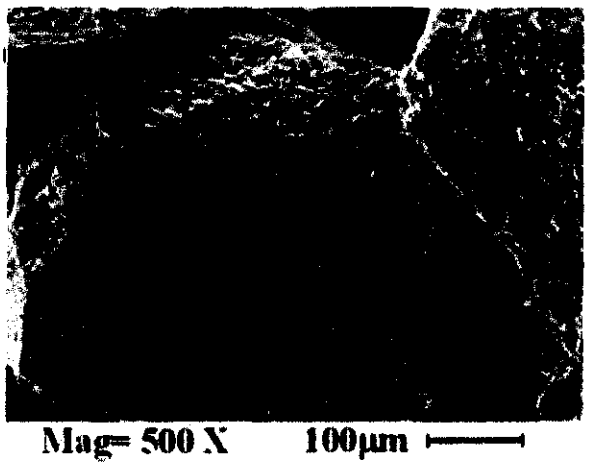
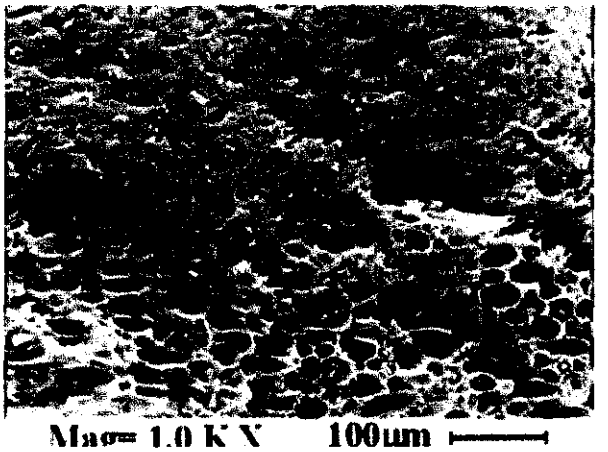
Raw Rice Husk	Treated Rice Husk
	

Figure 1. Pore Development For Raw Rice Husk and Treated Rice Husk

CHAPTER 3: METHODOLOGY

3.1 PROCEDURES

The methodology of the study can be divided into 4 major parts:

3.1.1 Preparation of rice husk

a) 300g of rice husk is collected and prepared. The rice husk are cleaned and washed with distilled water.
b) The rice husk will then be dried in the oven at temperature set at 80°C.
c) The dried rice husk is then grinded using a grinder.
d) Grinded rice husk is then sieved using sieve try sized 63 μm to obtain 63 μm size of rice husk.

The drying process is to remove any other unwanted volatile component and moisture that might still be present in the rice husk.

3.1.2 Treatment of raw rice husk

a) The rice husk is then mixed with a digesting agent which is 1.0M of sodium hydroxide (NaOH) in a beaker. A ratio if 1:10 of rice husk (gram) and digestion agent (milimeter) will be used which will be 100g of rice husk and 1000mL of NaOH.
b) Beaker containing sample is sealed using aluminium foil.
c) After 24 hours, the digested sample will then be filtered with distilled water.
d) The rice sample is then dried of in an oven at 80°C for 24 hours.
e) Finally, the sample is weighed.

3.1.3 Carbonization of rice husk

Treated rice husk is carbonized to eliminate non-carbon species and fix the carbon mass and basic carbon structure.

a) The treated rice husk is wrapped with aluminium foil placed in a crucible is put in the furnace once the temperature reaches 500°C.
b) The treated rice husk is carbonized around 2 hours in the presence of nitrogen. The temperature is set to 30°C once carbonizing is finished.
c) Samples are then taken out to be weighed and to calculate the percentage lost.

3.1.4 Adsorption study

The purpose of adsorption process is to observe the adsorption activities. Adsorption study is carried by mixing starting with 0.05g of sample in 25 ml of 150 ppm Pb(II) solution. Contact time is varied ranging from 5 minutes to 120 minutes in room temperature.

a) 25 ml of 150 ppm Pb(II) ion was prepared and mixed with 0.05g of carbonized rice husk in the vial.
b) The vial is place in the water bath shaker and left shaken at room temperature for 5 minutes.
c) The solutions are then filtered and the filtrate is taken to be analysed using AAS to check concentration of metal ion left in the filtrate.
d) Steps 1 to 3 are also conducted for various contact time ranging from 5,10,15,20, 30, 60, 90 and 120 minutes. These steps are again repeated with 0.1g, 0.15g, 0.2g and 0.3g of rice husk based activated carbon.

e) Graphs are then plotted to observe the effect of parameters varied on the adsorption activities.

3.1.5 Analyses

Samples before and after extraction study are analysed using several equipment listed below:

a) Field Emission Scanning Electron Microscope (FESEM):

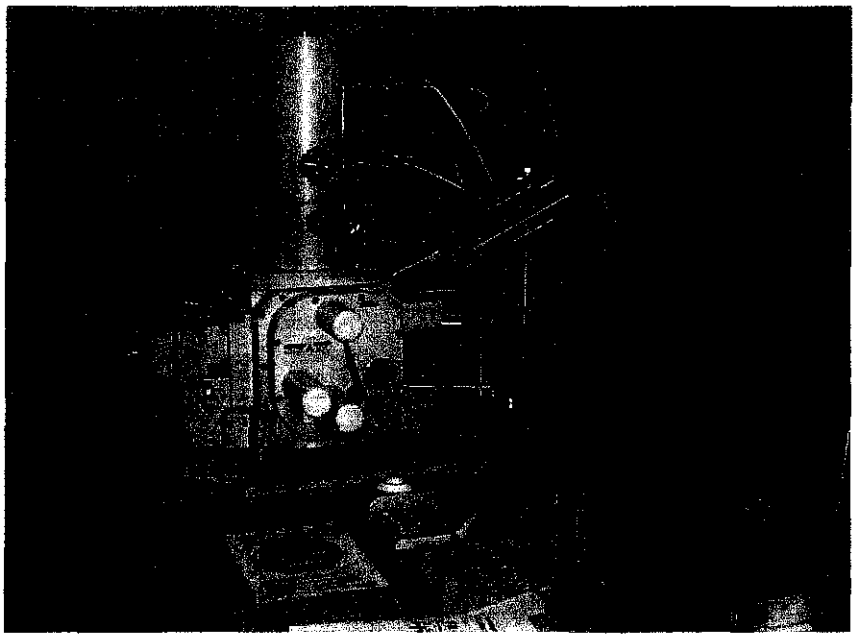


Figure 2. FESEM (Field Emission Scanning Electron Microscope)

This is basically a microscope that produces image of high resolution to observe development of pores. At high resolution, images can be highly magnified to get a better view for analysis with larger depth of focus. The sample preparation is easier since only SEM requires the sample to be conductive.

b) Fourier Transform Infrared(FTIR)

The main function of FTIR is to identify functional group of sample. FTIR spectrometer works by simultaneously collecting spectral data in a wide spectral range. The size of peak in the spectrum indicates the quantity of material present in the sample.

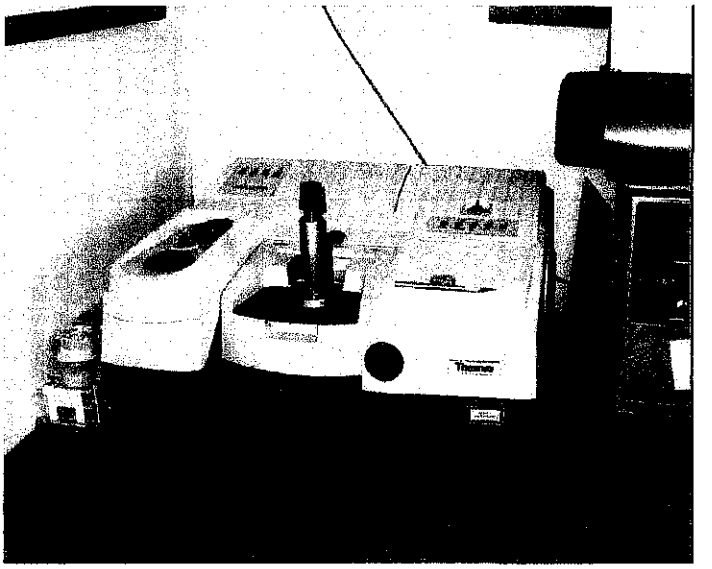


Figure 3. FTIR (Fourier Transform Infrared)

c) CHN Elemental Analyzer:

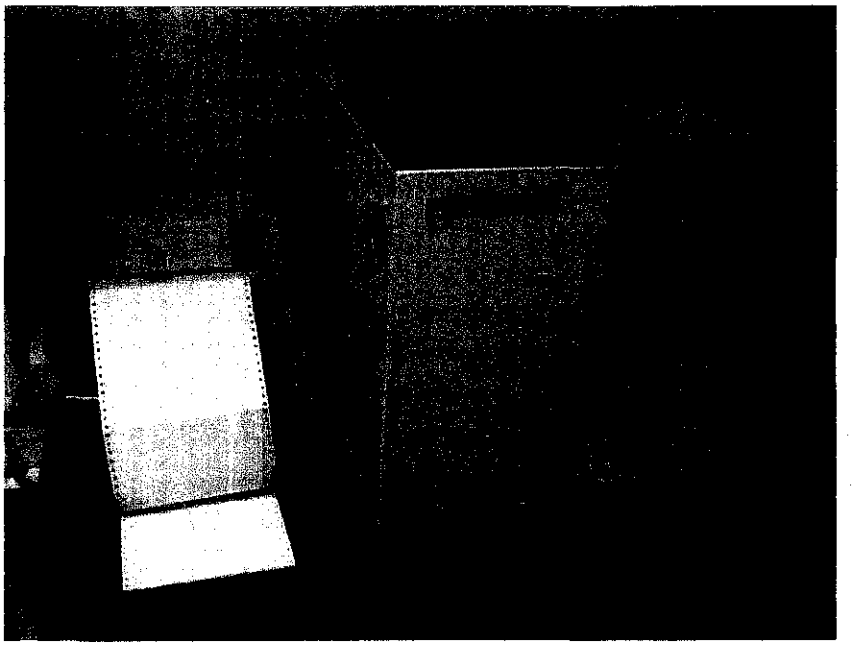


Figure 4: CHN Elemental Analyzer

CHN is used to determine carbon, hydrogen and nitrogen in organic matrices and other types of materials. The analysis is performed to provide carbonate and organic carbon and to obtain more information about organic matter composition.

d) X-Ray Diffraction (XRD):

Figure 5. XRD (X-Ray Diffraction)

XRD is used to measure diffraction beam intensity and d-spacings of chyrstalline materials. For this project, XRD is conducted to investigate the chrystalline and amorphous phases of carbon samples. XRD experiments are performed with 20 values ranging from 2° to 80°.

e) Energy-Dispersive X-Ray Spectroscopy (EDX/EDS):

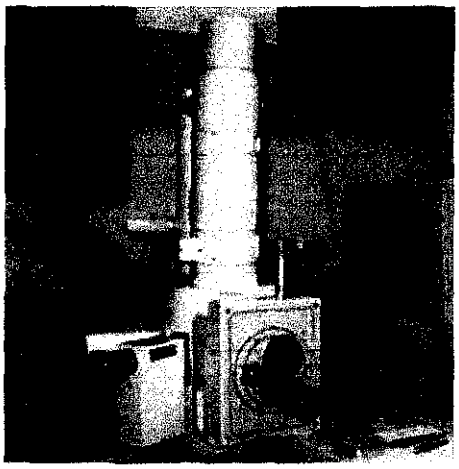


Figure 6. EDX (Energy-Dispersive X-Ray Spectroscopy)

EDX is used for elemental analysis or characterization of sample. This analytical device relies on sample investigation through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles.

f) Atomic Absorption Spectrometer(AAS):

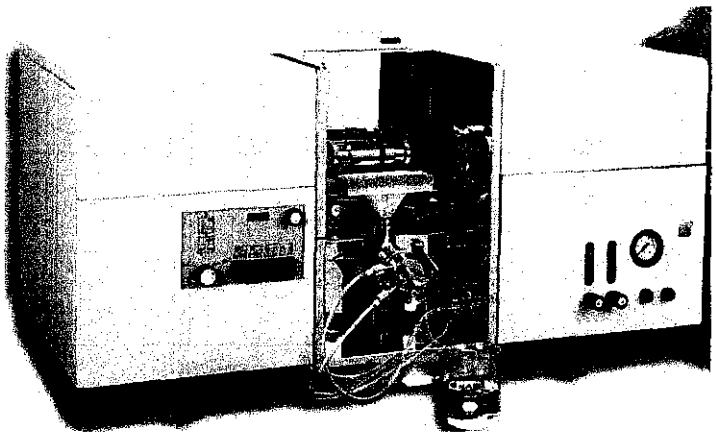


Figure 7. AAS (Atomic Absorption Spectrometer)

AAS is analytical equipment used to detect the metal ion concentration. It functions by providing accurate quantitative analyses for metals in water, rock or sediment solids. For this project, the purpose of using AAS is to determine the final concentration of metal ion in the filtrate.

g) BET surface analyser:

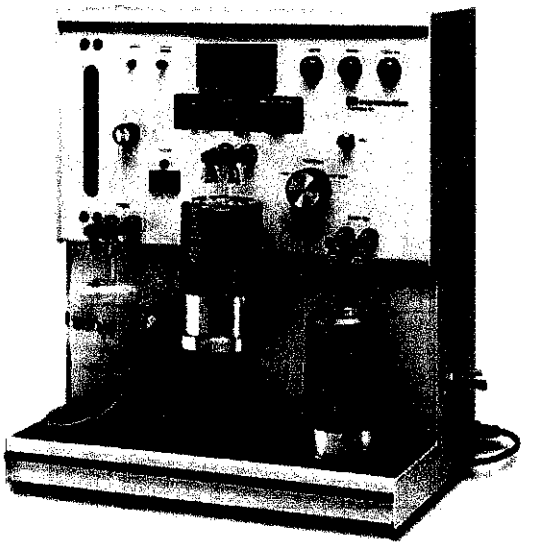


Figure 8. BET Surface Analyzer

BET helps to explain the physical adsorption of gas molecules in solid surface and serves a basis for important analysis technique to measure specific surface area of material.

Table 6. List of samples to be analysed:

No	Sample Name & Description	Label
1	Raw Rice Husk	RRH
2	Treated Rice Husk	TRH
3	Carbonized Rice Husk	CRH

3.2 EQUIPMENTS AND CHEMICALS

Lab equipment needed for this project are listed below:

Table 7. List of equipment

No	Equipment	Quantity	Remarks
1	FESEM	As per requirement	
2	BET	As per requirement	
3	FTIR	As per requirement	
4	CHN Elemental Analyzer	As per requirement	
5	XRD	As per requirement	
6	EDX	As per requirement	
7	AAS	As per requirement	
8	Blender	As per requirement	
9	Oven	As per requirement	
10	Furnace	As per requirement	With nitrogen flow
11	pH meter	As per requirement	Calibrated
12	Volumetric flask	As per requirement	
13	Siever	As per requirement	63 μm

The chemicals used in this project are listed below:

Table 8. List of chemicals

No	Chemical	Quantity	Remarks
1	Sodium Hydroxide, NaOH	As per requirement	
2	Lead Nitrate, $Pb(NO_3)_2$	As per requirement	Adsorbate
3	Distilled Water	As per requirement	

CHAPTER 4: RESULTS AND DISCUSSION

This section will further discuss the discoveries and discussion based on the results obtained from lab work preparation of activated carbon and the adsorption study of Pb(II) ion using rice husk based activated carbon.

4.1 Rice Husk Preparation

Initially the rusk husks were cleaned using distilled water, lots of paddy and other impurities were seen to be floating around on the water surface. For this, we placed the rice husk in a huge basin and start pouring distilled water into it for a more efficient cleaning method. The main reason for the cleaning process is to eliminate any traces of impurities that might contaminate the properties and composition of the rice husk. Once the rice husks were cleaned, we proceeded to dry them to remove any moisture content using ovens and simply drying them outside in open area. Afterwards, the rice husks were then grinded thoroughly and sieved using a 63 μm siever. The weight of the rice husk collected was 100g and the colour appears to be light brown.

4.2 TREATMENT OF RAW RICE HUSK WITH SODIUM HIDROXIDE (NaOH)

By using a ratio of 1:10 as discussed in the previous chapters, 100g of raw rice husks were treated with 1 L of 1.0M sodium hydroxide. The treatment of the rice husk was done for almost 24 hours and a stirrer was used during this period of time. Afterwards, the treated rice husk was washed with excessive distilled water to reduce the pH level. Observations of the change of colour and weight were recorded:

4.3 CARBONIZATION OF TREATED RICE HUSK

The carbonization process was conducted at 500°C with nitrogen flow as inert gas. An 11.05g of treated rice husk was carbonized at the specified temperature. The colour of the rice husk samples clearly changed into charcoal black. The weight of the sample has also decreased after the carbonization process, this is to be expected due to the loss of volatile materials as the process has undergone rapid heating. The results obtained are displayed below:

Table 9. Observation result of carbonized rice husk

Temperature (°C)	Color		Weight(g)	
	Before Carbonization	After Carbonization	Before Carbonization	After Carbonization
500	Light Brown	Dark Black	11.05	3.88

The pH level for the treated rice husk after washed with excessive distilled water was 7.05.

Table 10. Percentage weight loss after carbonization

Temperature (°C)	Color		Percentage Wight Loss (%)
	Before Carbonization	After Carbonization	
500	Light Brown	Dark Black	64.88

The weight for the samples after the carbonization has been reduced because other elements such oxygen and nitrogen were eliminated from the rice husk during the carbonization process.

4.4 SAMPLE CHARACTERIZATION

4.4.1 Field Emission Scanning Electron Microscope (FESEM)

Using Field Emission Scanning Electron Microscope (FESEM), 3 samples of rice husk were analysed:

1) Raw rice husk

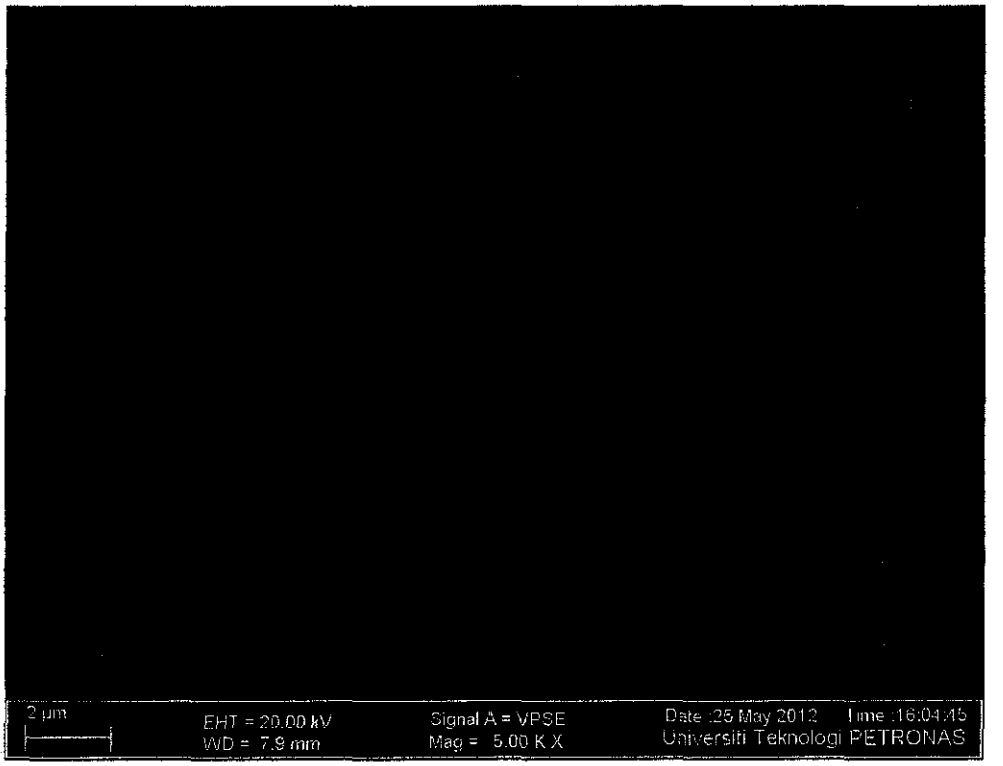


Figure 9. Raw Rice Husk (5000 Times Magnification)

2) Rice husk treated with 1.0M of sodium hydroxide

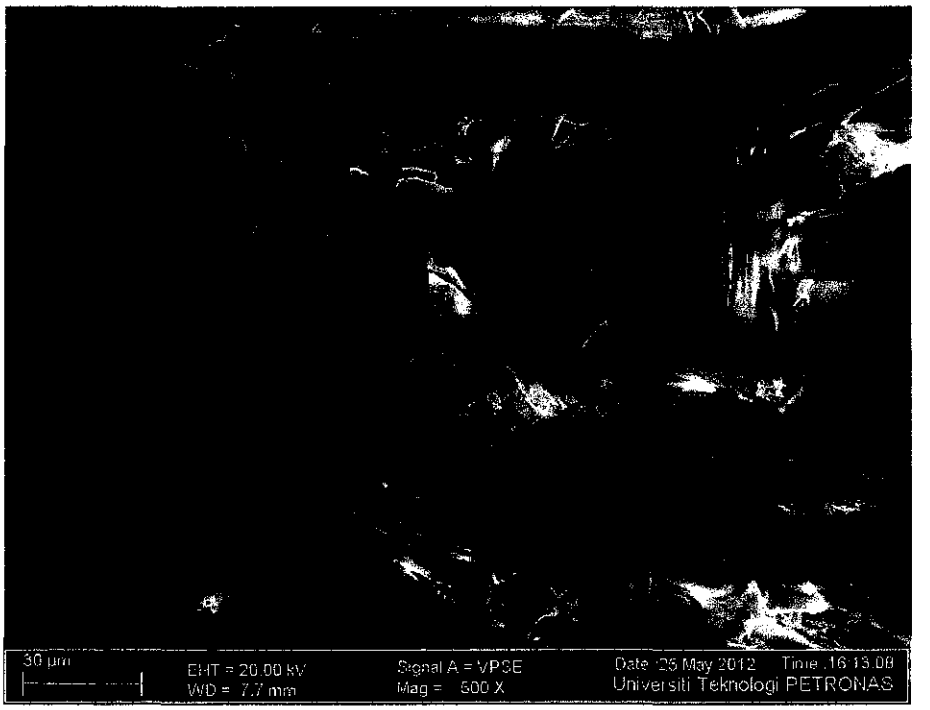


Figure 10. Rice husk treated with 1.0M NaOH (500 times magnification)

3) Carbonized Rice Husk at 500°C.

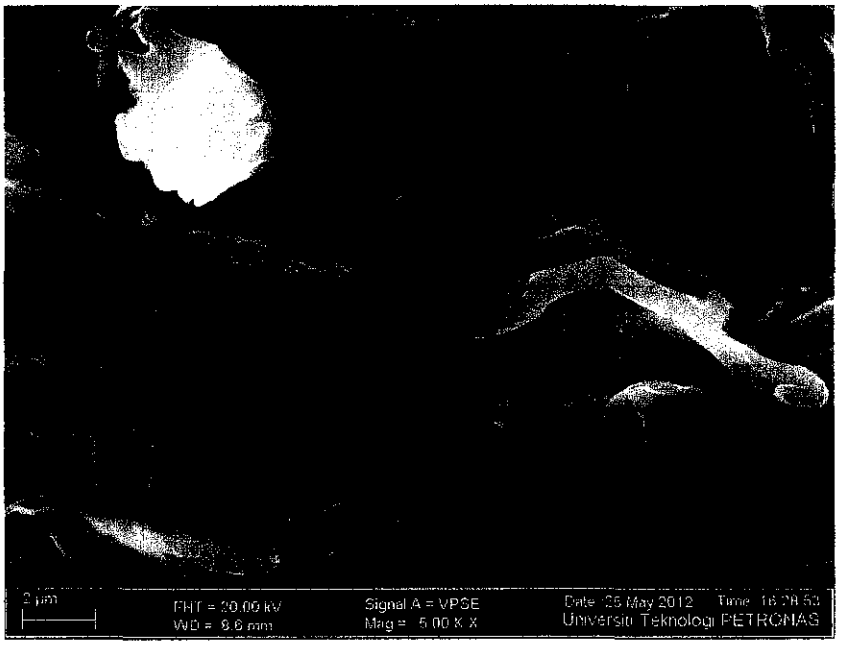


Figure 11. Carbonized Rice at 500 °C (5000 time magnification)

All the FESEM micrographs of raw rice husk, rice husk treated with sodium hydroxide and carbonized rice are displayed in Figure 9, 10 and 1. Different morphology has been obtained for each carbon sample following the development of the pores of rice husk that has gone through different processes of treatment with sodium hydroxide and carbonization process. Figure 9 indicates that the rice rusk husk image shows no sign of pores. Figure 4 shows the FESEM micrograph of rice husk treated 1.0M of sodium hydroxide which compared to raw rice husk is observed to have better pores development.

Figure 11 displays the carbonized rice husk at 500°C. Based on the observation for this image, developments of pores have increased and shown to have more pores compared to previous samples. This can be explained by the removal of volatile materials and non-carbon elements which were trapped in the pores of rice husk during carbonization process. FESEM micrographs have clearly shown the development of pores of rice pores for each processes and researches have stated that pores development would provide better adsorption capability on metal ions that can be trapped into pores structures.

4.4.2 Fourier Transform Infrared (FTIR)

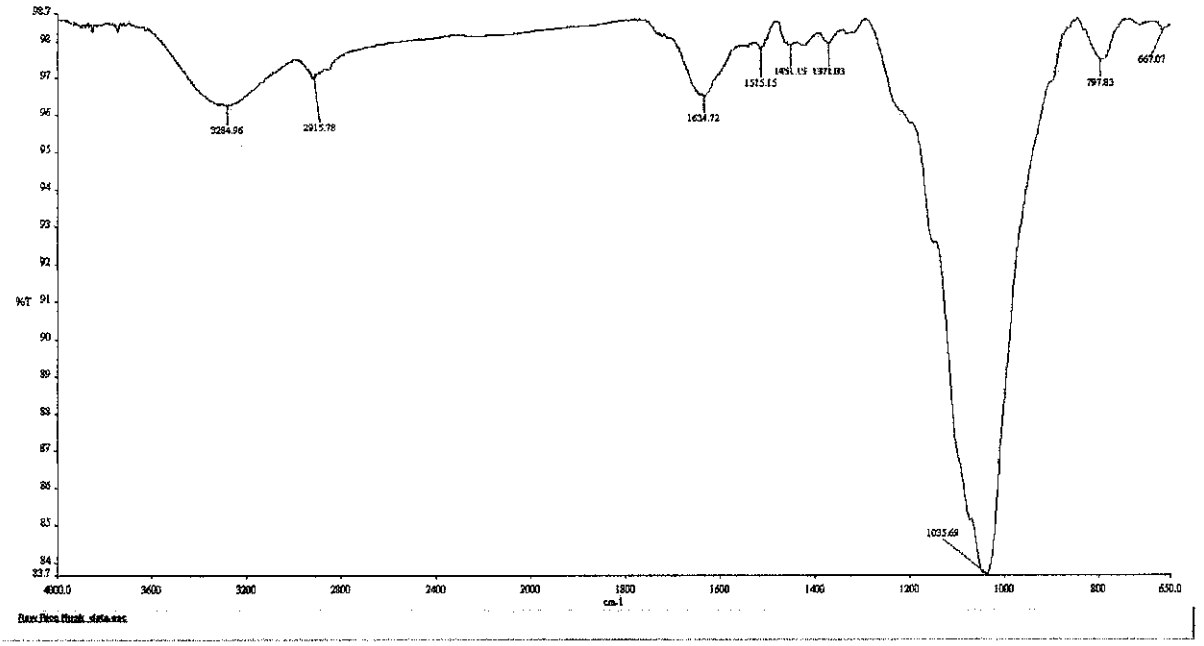


Figure 12. FTIR Spectra RRH

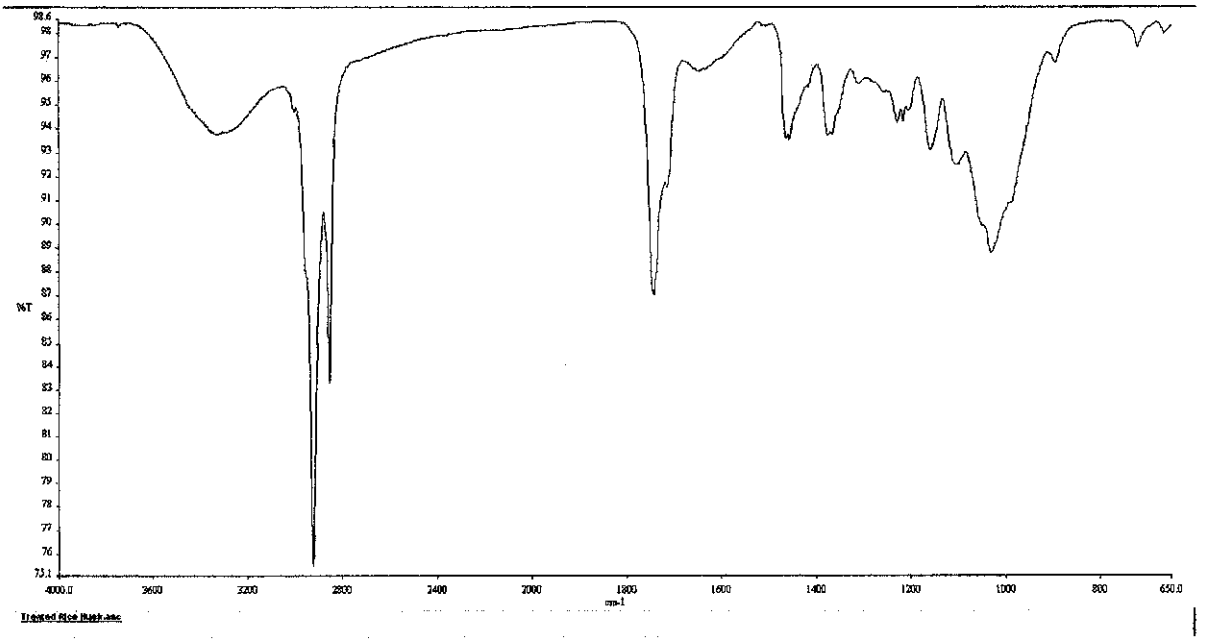


Figure 13. FTIR Spectra TRH

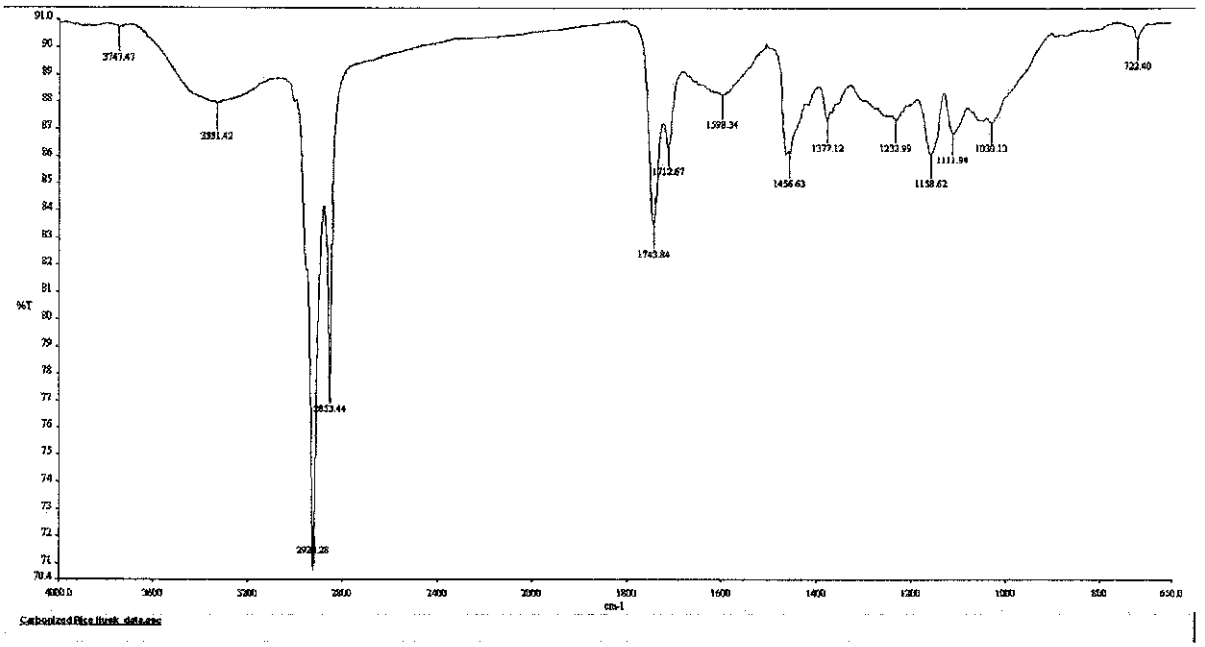


Figure 14. FTIR Spectra CRH

FTIR is a device that can be used to properly identify the characteristic of functional groups. FTIR provides information on the chemical structure of materials of the analysed rice husk samples. Figure 12 and 13 shows the IR spectrum of raw rice husk and treated rice husk, respectively. Significant difference is present in the spectra of these samples, both demonstrating number of peaks of functional group responsible for sorption. Referring to figure, RRH shows a wide band at around 1035 cm-1. The C-O stretch bond of alcohol groups can be assigned to this band. Weak band at 3284 cm-1 can be assigned to –OH stretching vibration mode of hydroxyl functional groups including hydrogen bonding of chemisorbed water. The bond at 1634 cm-1 corresponds to C=O stretching vibrations that could be due to lignin aromatic and hemicelluloses groups.

Figure 13 and 14 shows the treated rice husk and carbonized rice husk samples. Both seems to have similar peeks at around 2920 cm-1 and 2850 cm-1 which may be attributed to C-H stretching vibrations in alkanes, carbon is bonded with hydrogen. For carbonised rice husk sample, intensity of certain band was reduced at higher temperature, this indicates the vaporization of organic matter and how carbon content increases as the temperature rises. Based on the trend displayed, it can be concluded

carbonization helps to produce higher carbon content in the carbonized rice husk sample.

4.4.3 Thermogravimetric Analyzer (TGA)

For TGA, the reduction of weight loss for test sample is recorded while the samples are being heated at a costant in a suitable environment. The weight loss over specific temperature ranges indicates the sample composition, which also includes inert filler and volatiles. Various components of the sample start to disintegrate as the temperature rises and weight percentage for each can be measured. Figure 15 display the TG curves of the weight percent for raw rice husk(RRH), treated rice husk (TRH) and carbonized rice husk(CRH).

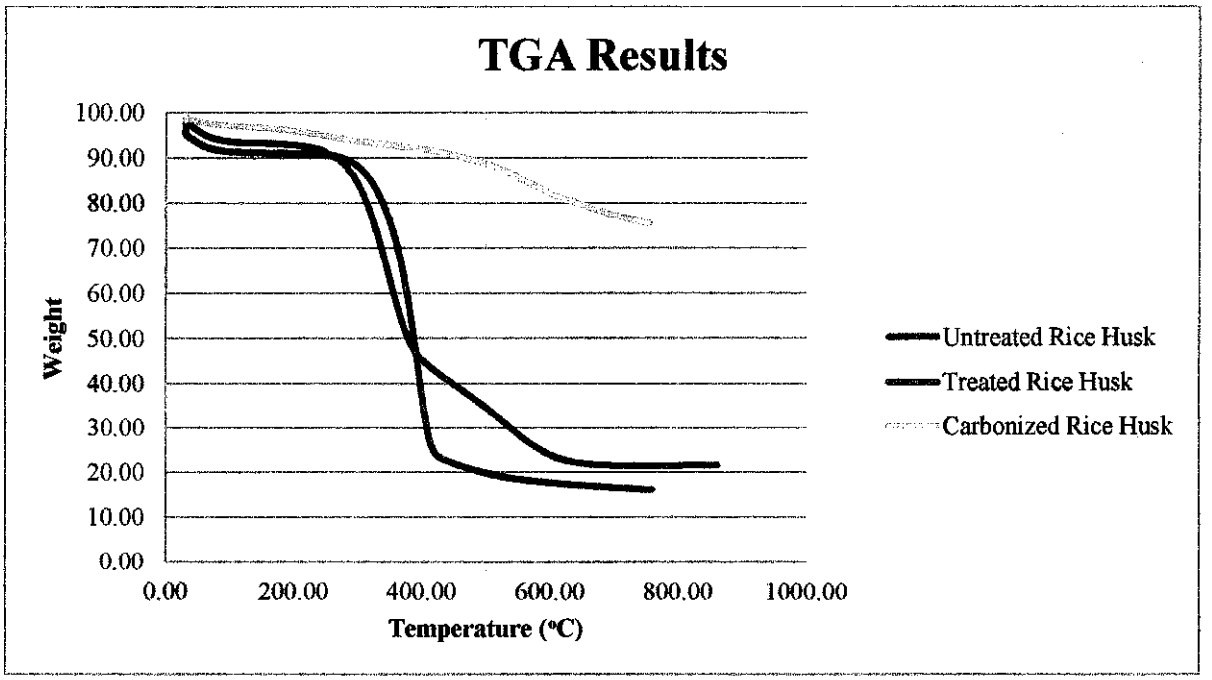


Figure 15. TG Thermograph of RRH, TRH and CRH

The TG curves shows the loss of mass for raw rice husk (RRH), treated rice husk (TRH) and carbonized rice husk (CRH) which can be divided into a few stages since it occurs at 3 different temperature zones. According to the results obtained, the curves show a small lost for temperature around 200°C which could be due to elimination of water moisture. From 200 to 400°C, greater loss of mass occurs within this range of temperature which indicates carbonization that eliminates any trace of trace of tars and volatile matters. From 400°C and onwards shows structure decomposition of higher stability. However, for CRH, there is not much of mass lost since most of them were eliminated during treatment with sodium hydroxide and carbonization process.

4.4.4 CHN Elemental Analyzer

Three samples were sent to be analysed using CHN Elemental Analyzer which are raw rice husk, rice husk treated with 1.0M sodium hydroxide and carbonized rice husk. The analysis results are measured by the weight percentage (wt%) as displayed below:

Table 11. Table of CHN analysis

		Weight Percent (%)		
Sample	Label	Carbon	H_2	N_2
Raw Rice Husk	RRH #1	34.07	4.652	1.663
	RRH #2	30.41	3.711	1.413
Treated Rice Husk	TRH #1	38.41	4.371	0.698
	TRH #2	40.09	4.375	0.703
Carbonized Rice Husk	CRH #1	65.73	4.022	1.122
	CRH #2	65.10	3.699	1.038

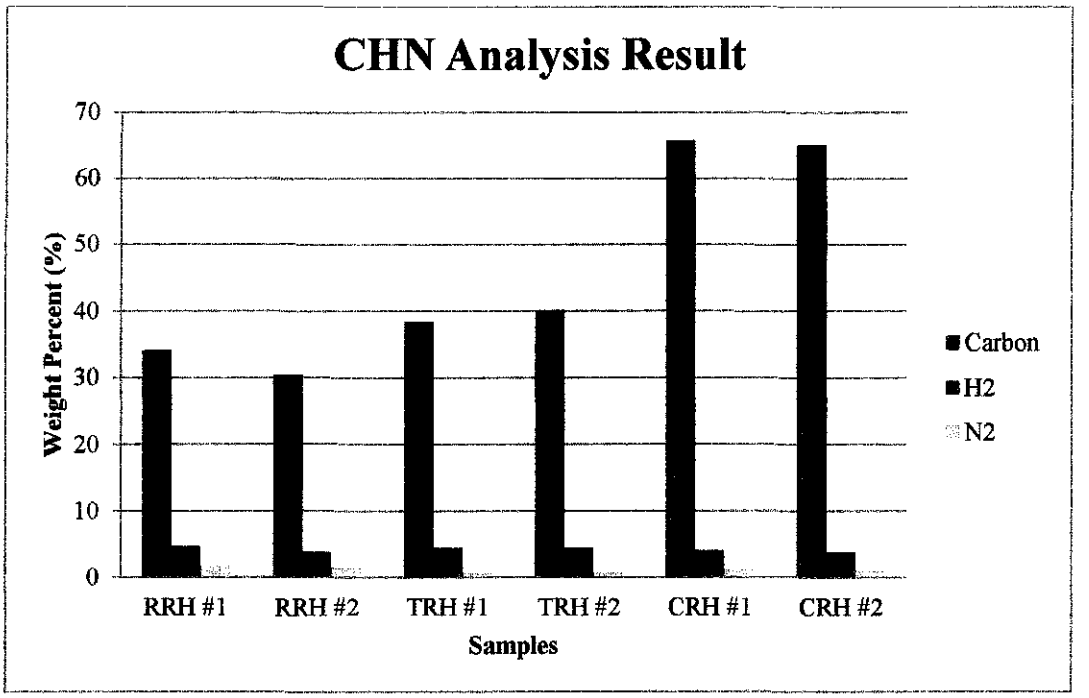


Figure 16. CHN Analysis Result

According to the results, it seems that there is an increase of carbon element percentage after treatment with sodium hydroxide and carbonization process. Nitrogen and hydrogen percentage however do not follow the same trend as both decreases. The decreased for both elements happened during the process of treatment with sodium hydroxide and carbonization process, therefore increasing the percentage weight of carbon. Carbonized rice husk sample indicates the highest percentage of carbon since most volatile matters were removed during carbonization process.

4.4.5 X-Ray Diffraction (XRD)

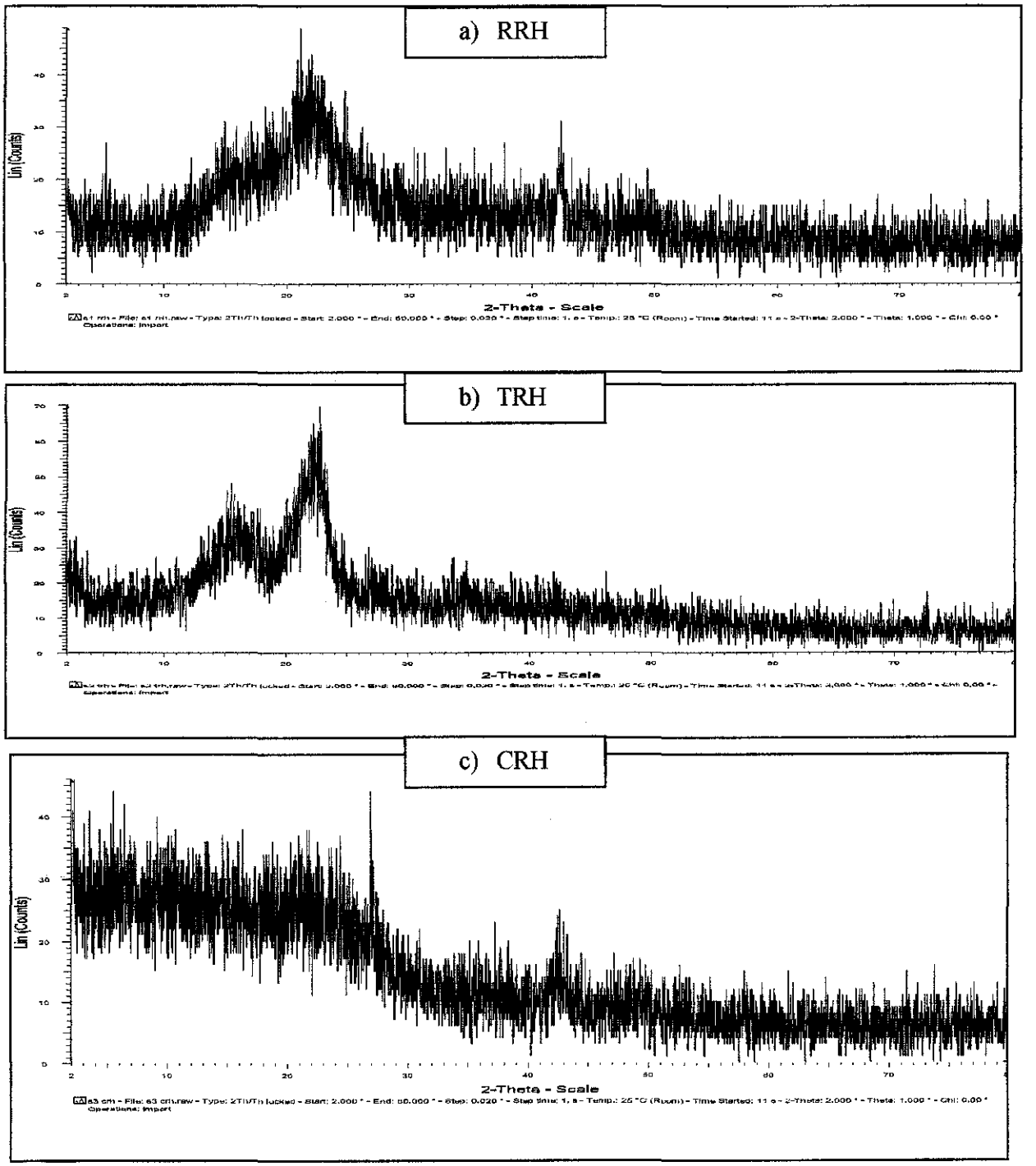


Figure 17. XRD Curves for (a) Raw Rice Husk (RRH (b) Treated Rice Husk (TRH) (c) Carbonized Rice Husk (CRH)

Figure 37 displays the XRD curves for all 3 samples of raw rice husk, treated rice husk and carbonized rice husk. According to the results, the differences of each characteristic for each sample can be identified. For XRD analysis, crystallinity shows narrow peaks of diffraction and amorphous component has a very broad peak.

The broad peak centered at the 2Θ angle of 22° is typical of silica for figure 37 (a) and (b) which are raw rice husk and treated rice husk samples that are amorphous. The same pattern is obtained with carbonized rice husk. There seems to be broad and sharp peak centered around 2Θ angle of 22° and 16° for both figures 37 (a) and (b) which shows that both contain mixture of amorphous and crystalline phases of silica. Chrystalline phases of silica are identified as chystobalite and tridymite (Yalcin N. & Sevinc V., 2001).

4.4.6 Atomic Absorption Spectrophotometer (AAS)

Solution of Pb(II) ion changed from colourless to dark black when rice husk-based activated carbon was placed into the solution during shaking process using bath shaker. After filtering the solution, the filtrate solution was analysed using Atomic Absorption Spectrophotometer (AAS) to check the final concentration of Pb(II) ion. Standard solutions of Pb(II) ions with varying concentration were prepared to acquire the calibration curve. The calibration curve achieved by preparation of standard solution at 0, 4, 8 and 16 ppm is displayed in figure #.

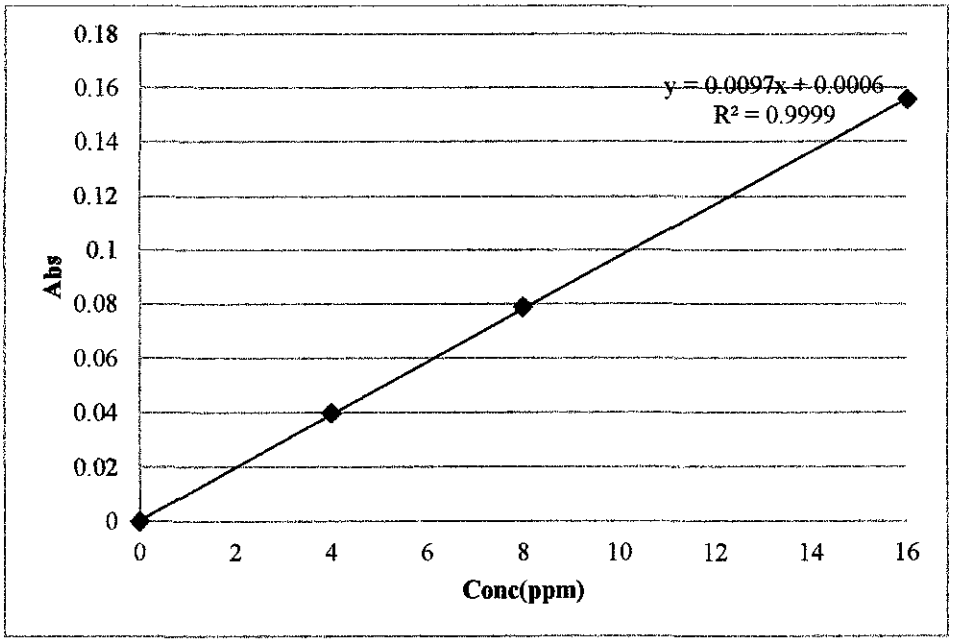


Figure 18. AAS calibration curve with $R^2 = 0.9999$

Based on the graph above, the R^2 value represents the deviation of data collection in comparison to the straight line (linear). The R^2 value obtained from graph was 0.9999 which shows that the standard solution was almost perfect as the value was really close to 1.

4.5 ADSORPTION STUDY

The adsorption study was conducted at different time interval (5, 10, 15, 20, 30, 60, 90 and 120 minutes) starting 0.05g of activated rice husk activated carbon and repeated with 0.10g, 0.15g, 0.20g and 0.30g. The contact time refers to duration of the adsorbent mixed and left in the solution of adsorbate. For this research, activated carbon is referred as the adsorbent and Pb(II) as the adsorbate. The contact time is the duration of activated carbon starting with 0.05g mixed with 25mL of 150ppm of Pb(II) ion solution left in the bath shaker.

Table 12. Experimental data for effect of contact time (0.05g of rice husk activated carbon)

Activated Carbon Weight(g)	Adsorption Contact Time (min)	Initial Concentration (ppm)	Final Concentration (ppm)	Percent Metal Uptake (% removal)	Adsorption Capacity
0.05	5	150	71.53	52.31	39.235
	10	150	71.08	52.61	39.46
	15	150	70.9	52.73	39.55
	20	150	70.6	52.93	39.7
	30	150	70.54	52.97	39.73
	60	150	70.18	53.21	39.91
	90	150	70.08	53.28	39.96
	120	150	70.03	53.31	39.985

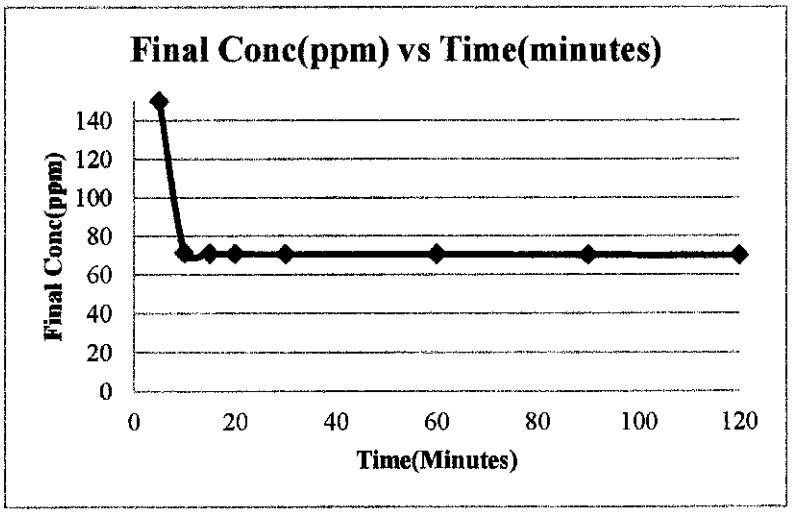


Figure 19. Effect of contact time on percent uptake (0.05g of rice husk based activated carbon)

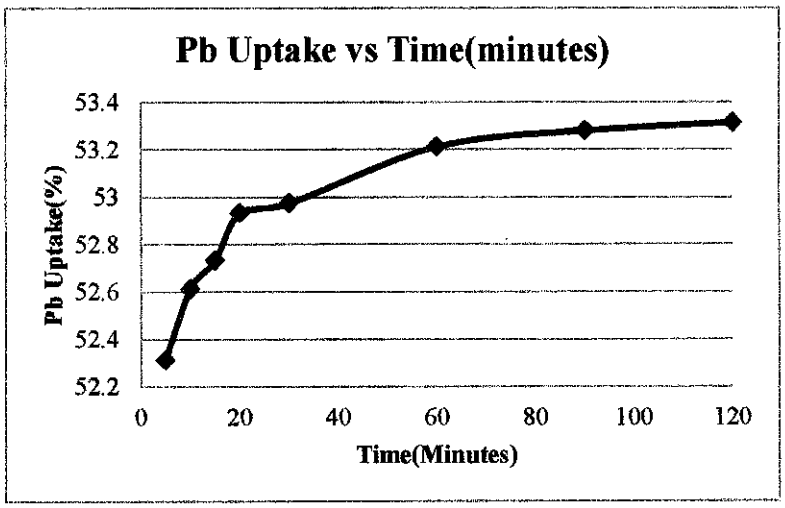


Figure 20. Effect of contact on lead uptake (0.05g of rice husk based activated carbon)

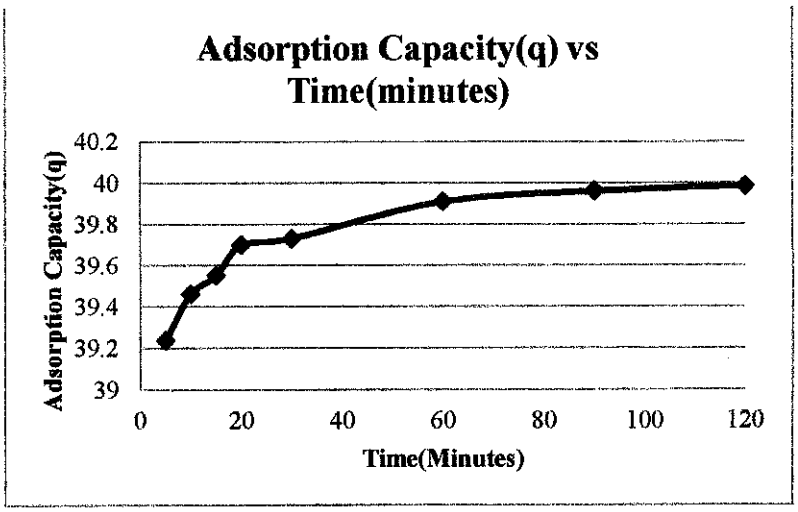


Figure 21. Effect of contact time on adsorption capacity (0.05g of rice husk based activated carbon)

Table 13. Experimental data for effect of contact time (0.1g of rice husk activated carbon)

Activated Carbon Weight(g)	Adsorption Contact Time (min)	Initial Concentration (ppm)	Final Concentration (ppm)	Percent Metal Uptake (% removal)	Adsorption Capacity
0.1	5	150	69.92	53.38	20.02
	10	150	69.78	53.48	20.055
	15	150	69.54	53.64	20.115
	20	150	69.51	53.66	20.1225
	30	150	69.44	53.70	20.14
	60	150	69.26	53.82	20.185
	90	150	69.22	53.85	20.195
	120	150	69.06	53.96	20.235

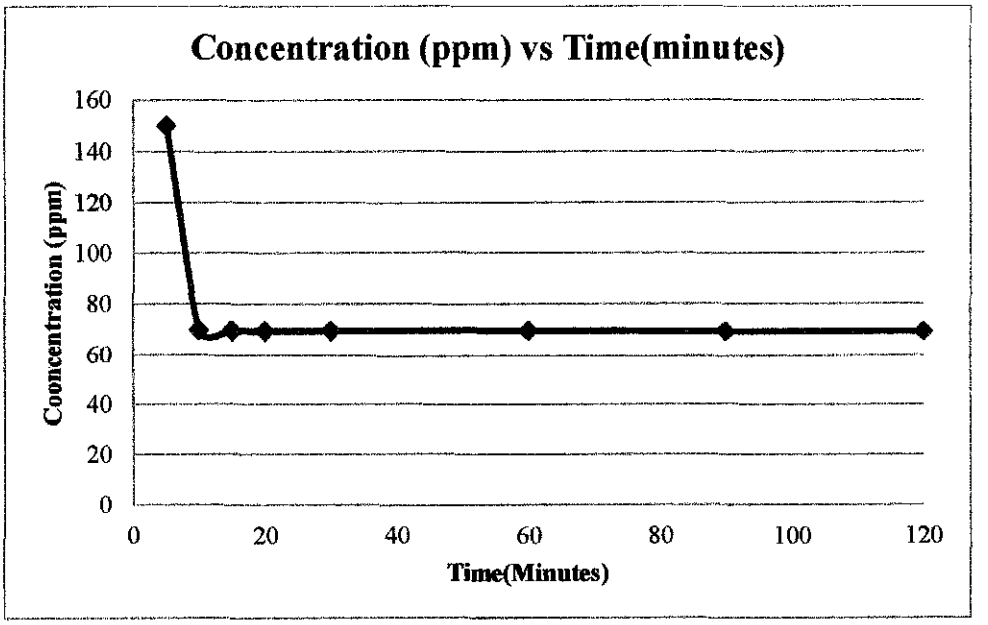


Figure 22. Effect of contact time on concentration of Pb(II) ion solution (0.1g of rice husk based activated carbon)

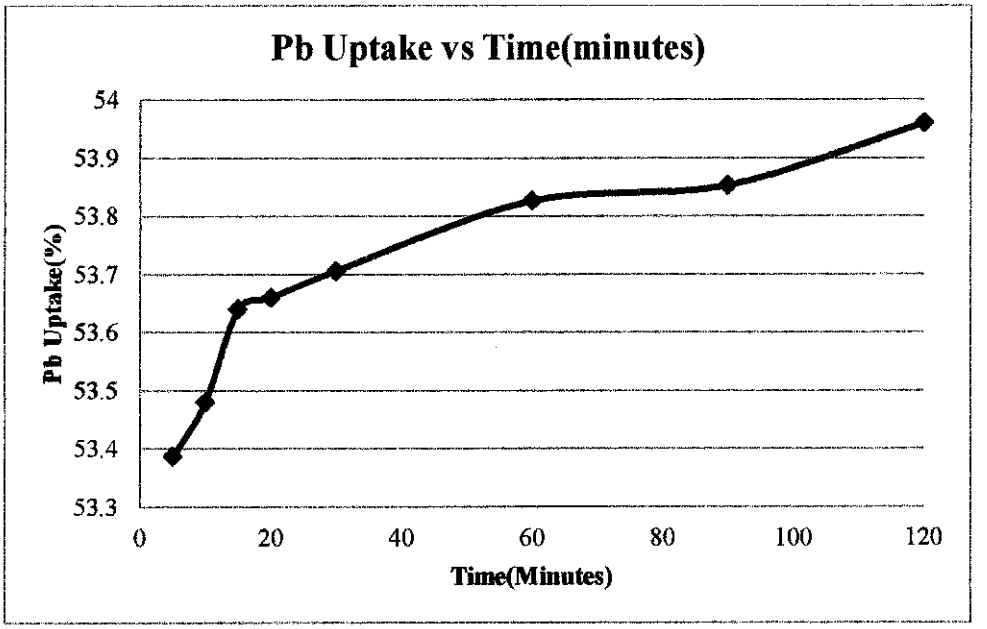


Figure 23. Effect of contact time on percent lead uptake (0.1g of rice husk activated carbon)

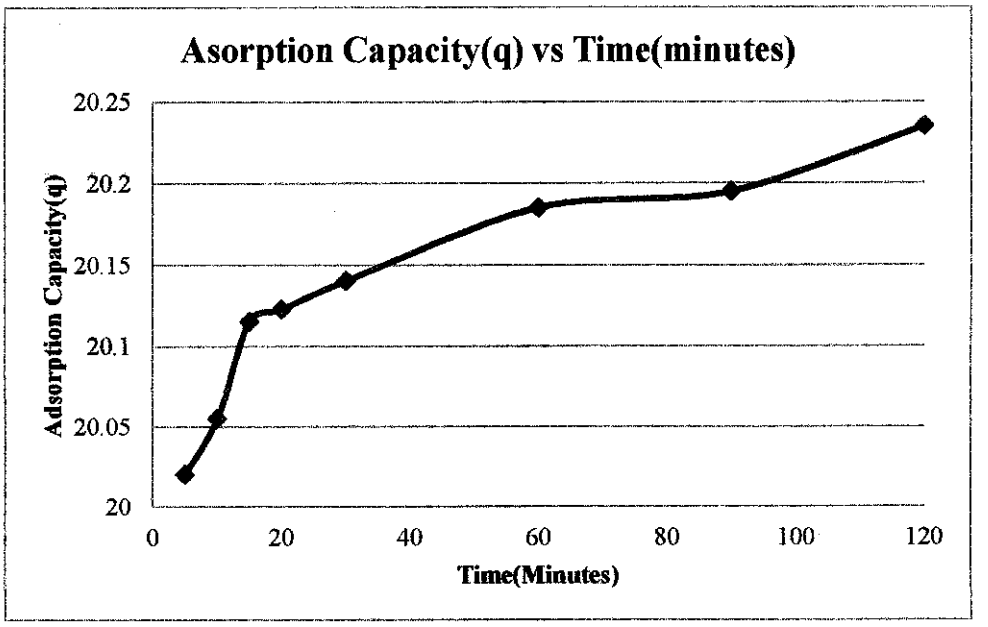


Figure 24. Effect of contact time on adsorption capacity (0.1g of rice husk activated carbon)

Table 14. Experimental data for effect of contact time (0.15g of rice husk activated carbon)

Activated Carbon Weight(g)	Adsorption Contact Time (min)	Initial Concentration (ppm)	Final Concentration (ppm)	Percent Metal Uptake (% removal)	Adsorption Capacity
0.15	5	150	69.74	53.50	13.37
	10	150	69.54	53.64	13.41
	15	150	69.31	53.79	13.44
	20	150	68.88	54.08	13.52
	30	150	68.81	54.12	13.53
	60	150	68.75	54.16	13.54
	90	150	68.68	54.21	13.55
	120	150	68.19	54.54	13.63

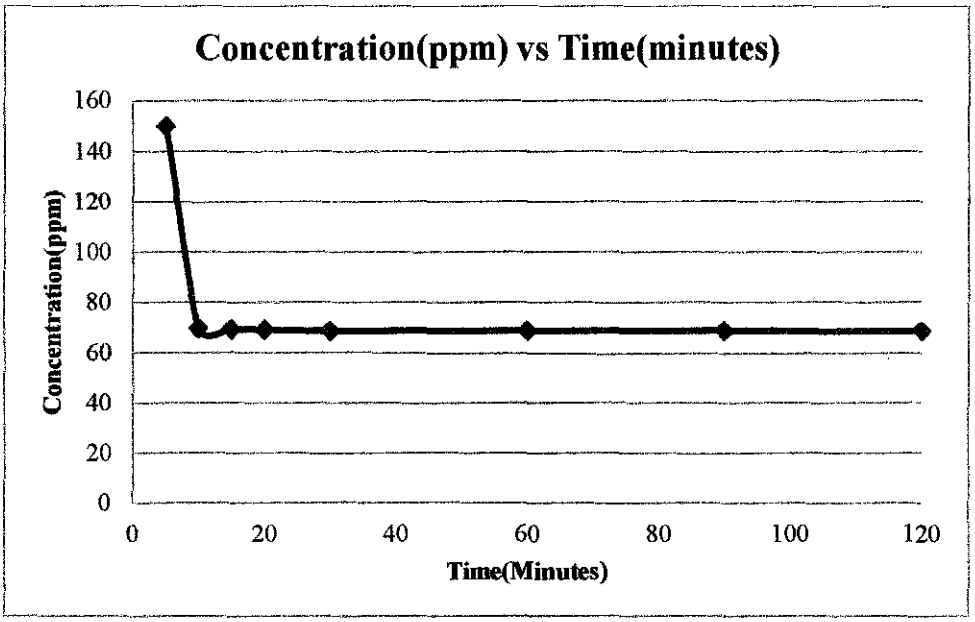


Figure 25. Effect of contact time on concentration of Pb(II) ion solution (0.15g of rice husk activated carbon)

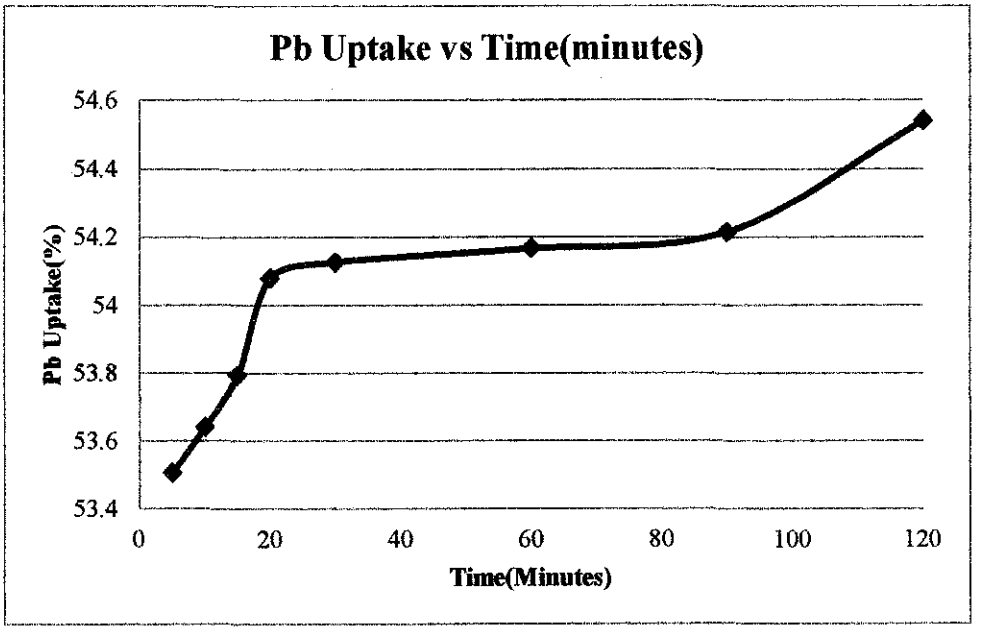


Figure 26. Effect of contact time on percent lead uptake (0.15g of rice husk activated carbon)

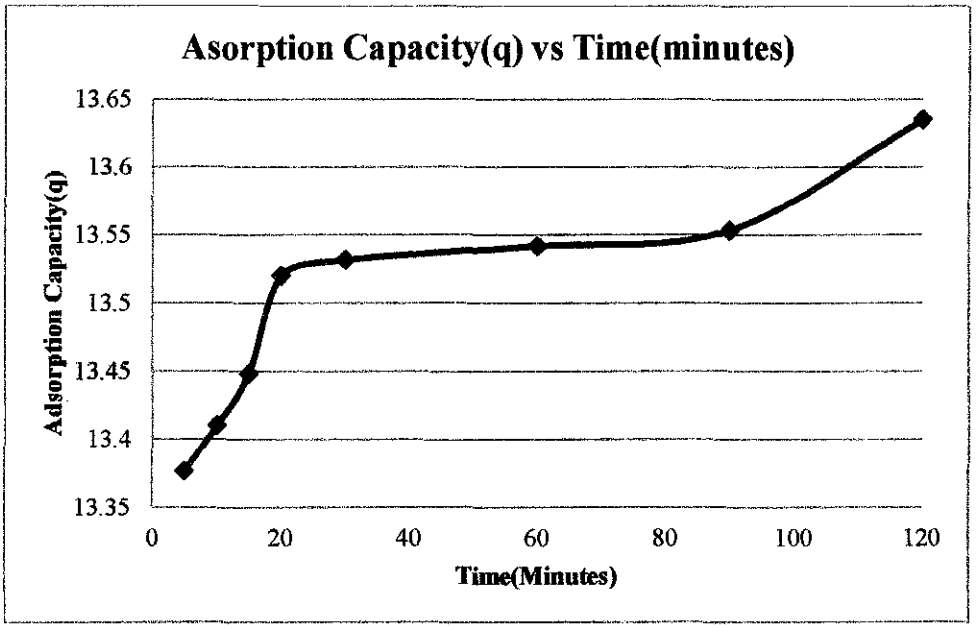


Figure 27. Effect of contact time on adsorption capacity (0.15g of rice husk activated carbon)

Table 15. Experimental data for effect of contact time (0.2g of rice husk activated carbon)

Activated Carbon Weight(g)	Adsorption Contact Time (min)	Initial Concentration (ppm)	Final Concentration (ppm)	Percent Metal Uptake (% removal)	Adsorption Capacity
0.20	5	150	68.67	54.22	10.16
	10	150	68.41	54.39	10.19
	15	150	68.33	54.44	10.20
	20	150	68.28	54.48	10.21
	30	150	68.13	54.58	10.23
	60	150	67.93	54.71	10.25
	90	150	67.6	54.93	10.30
	120	150	67.54	54.97	10.30

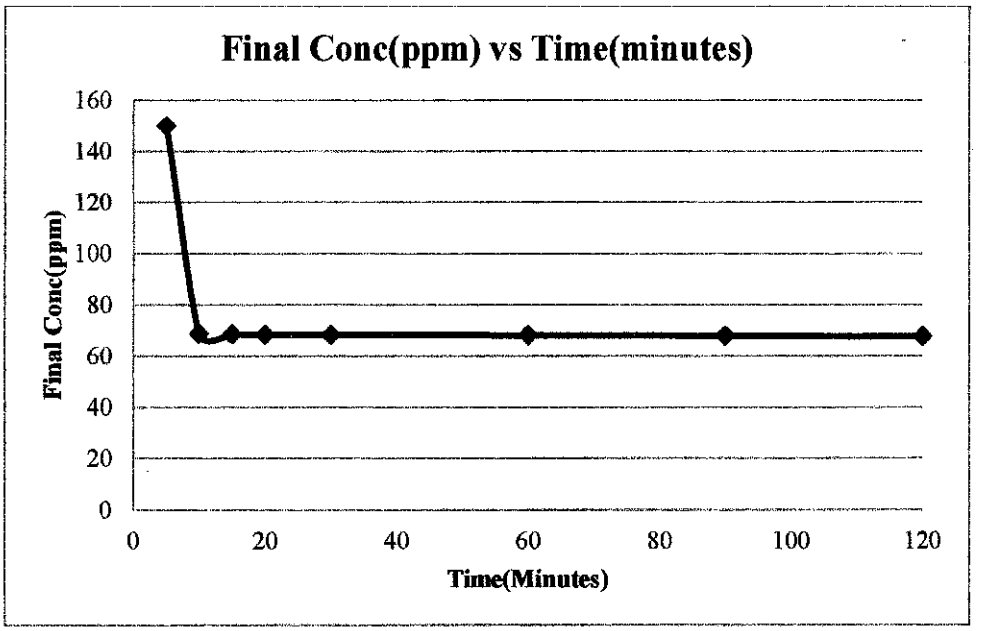


Figure 28. Effect of contact time on concentration of Pb(II) ion solution (0.2g of rice husk activated carbon)

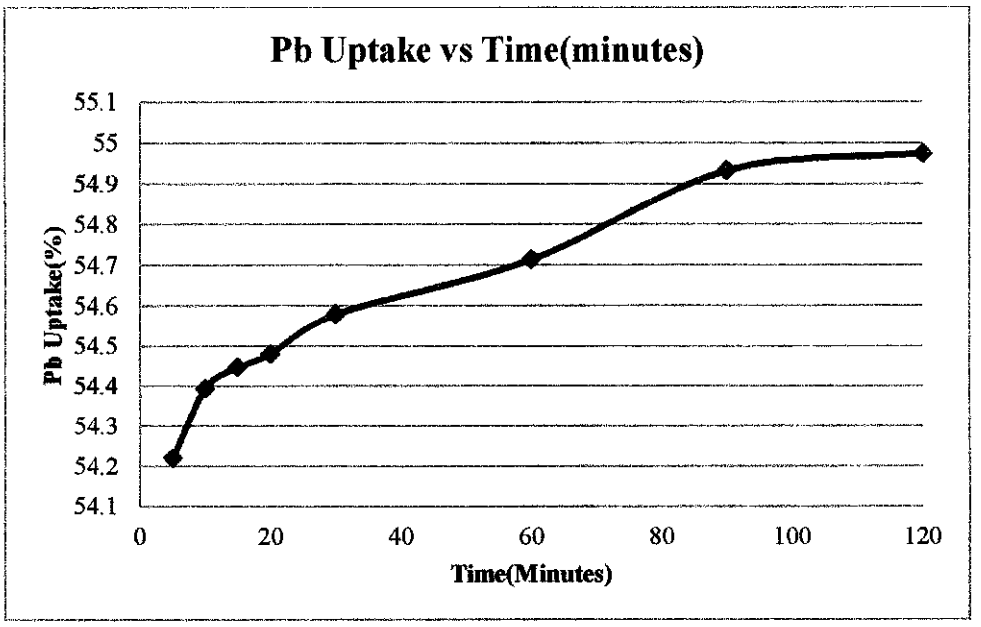


Figure 29. Effect of contact time on percent lead uptake (0.2g of rice husk activated carbon)

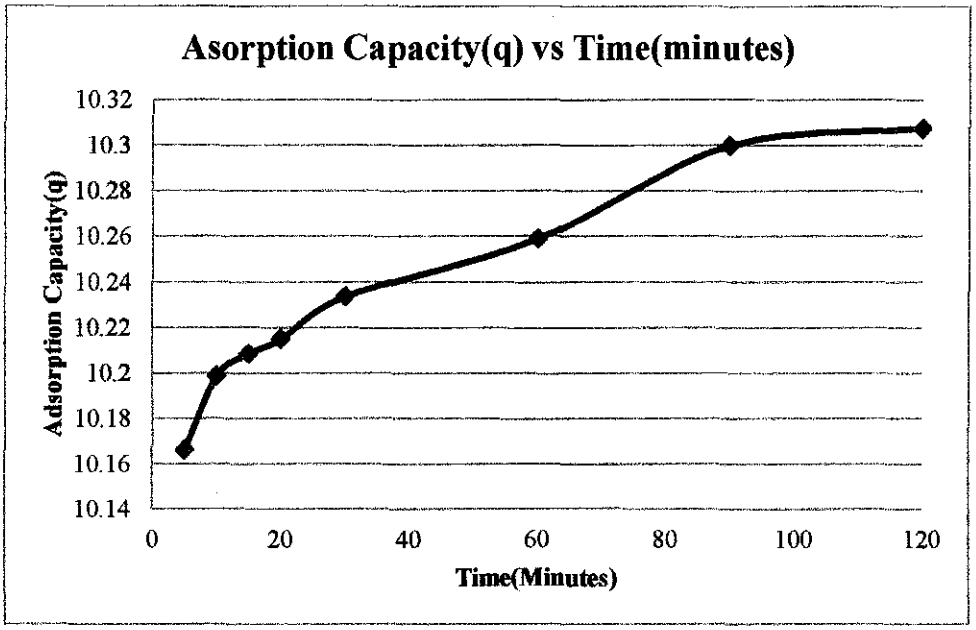


Figure 30. Effect of contact time on adsorption capacity (0.2g of rice husk activated carbon)

Table 16. Experimental data for effect of contact time (0.3g of rice husk activated carbon)

Activated Carbon Weight(g)	Adsorption Contact Time (min)	Initial Concentration (ppm)	Final Concentration (ppm)	Percent Metal Uptake (% removal)	Adsorption Capacity
0.30	5	150	67.67	54.88	6.86
	10	150	67.42	55.05	6.88
	15	150	67.3	55.13	6.89
	20	150	66.96	55.36	6.92
	30	150	66.94	55.37	6.92
	60	150	66.91	55.39	6.92
	90	150	66.86	55.42	6.92
	120	150	66.8	55.46	6.93

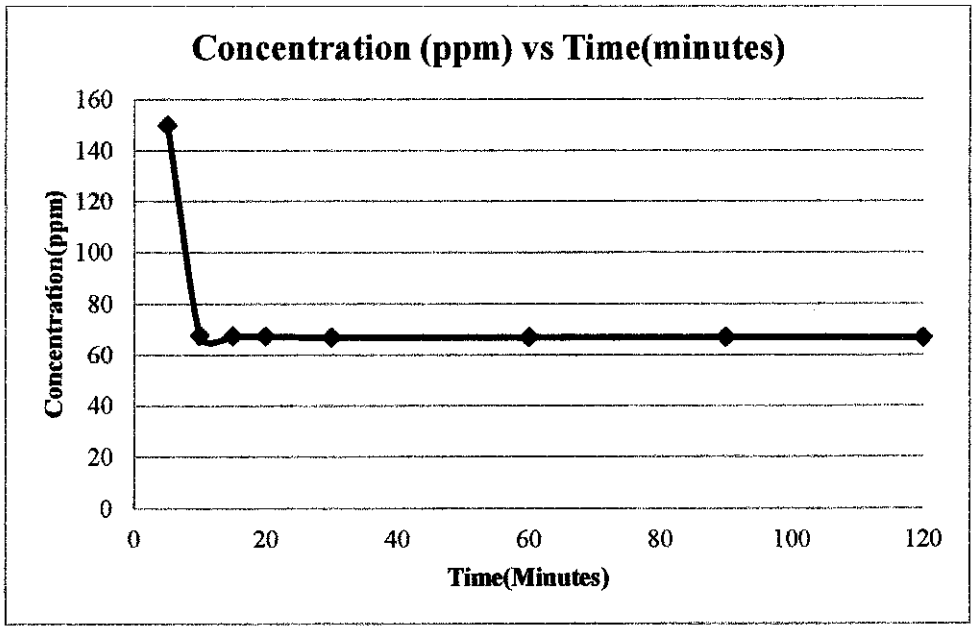


Figure 31. Effect of contact time on concentration of Pb(II) ion solution (0.3g of rice husk activated carbon)

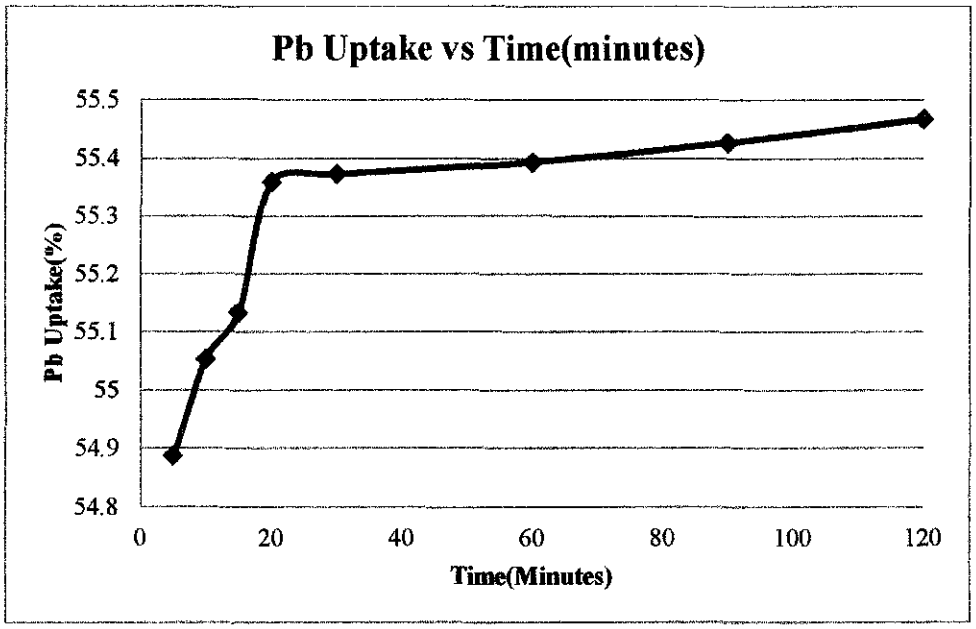


Figure 32. Effect of contact time on percent lead uptake (0.3g of rice husk activated carbon)

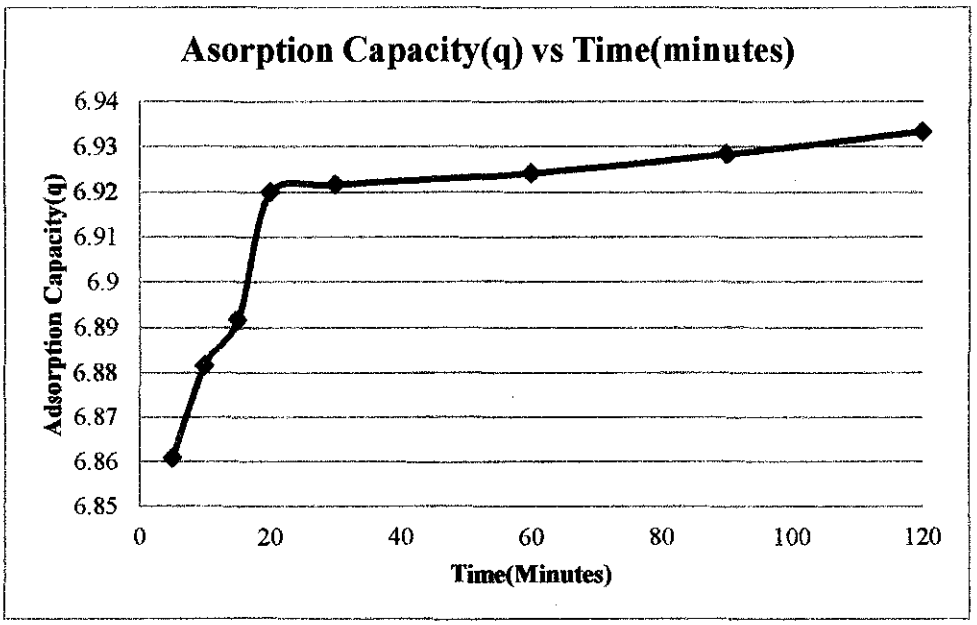


Figure 33. Effect of contact time on adsorption capacity (0.3g of rice husk activated carbon)

Figures 20 to 34 displays the percent lead uptake and adsorption capacity for different rice husk mass at varied contact time. According to the results, it can be observed from figure 21 and 22 that the percent lead uptake and adsorption capacity increases as adsorption contact time increases until the system reaches equilibrium. It seems that the maximum removal of Pb(II) occurred mostly at around 60 minutes which is the equlibrium. The same pattern is also displayed from figure 33 and 34, however removal of Pb(II) ion reaches maximum at the time of equilirbrium which is at 30 minutes. For figure 25, 27 ,28, 30 and 31, the maximum removal of Pb(II) seem to reached equilibrium at around 60 minutes with a minor change in the extent of adsorption after equilibrium.

All rice husk-based activated carbon samples have shown similar trend as the contact time keeps increasing. Usage of increasing weight of activated carbon does indicate higher percentage of metal uptake. The highest percentage of metal uptake obtained from this research is around 55.46% at 120 minutes of adsorption contact time using 0.3g of activated carbon. This is because higher contact time allows more time for rice husk-based activated carbon to adsorb metal ion.

4.5.1 Adsorption Analysis

The process of adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate adsorbed on the surface of adsorbent and pressure at constant temperature. Different adsorption isotherms that will be used for this study would be Freundlich and Langmuir Isotherm.

4.5.2 Langmuir Isotherm

This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. It makes assumptions such as monolayer adsorption and constant adsorption energy. The equation for Langmuir isotherm is displayed below:

$$q = \frac{q_{max} b C_f}{(1 + bC_f)}$$

This is linearized to

$$\frac{1}{q} = \frac{1}{q_{max}} + \left(\frac{1}{b.q_{max}}\right)(C_f)$$

q_{max} and b are the Langmuir constants

4.5.3 Freundlich Isotherm

This model deals with surface heterogeneity, exponential distribution of active sites of sorbent and energies towards sorbent. It is able to describe the experimental data well on a usual basis. The Freundlich equation of adsorption isotherm is displayed below:

$$q = K(C_e)^{1/n}$$

This is linearized to:

$$\log q = \log K + \left(\frac{1}{n}\right) \log C_e$$

q is amount adsorbed per unit mass of adsorbent and C_e is the equilibrium concentration.

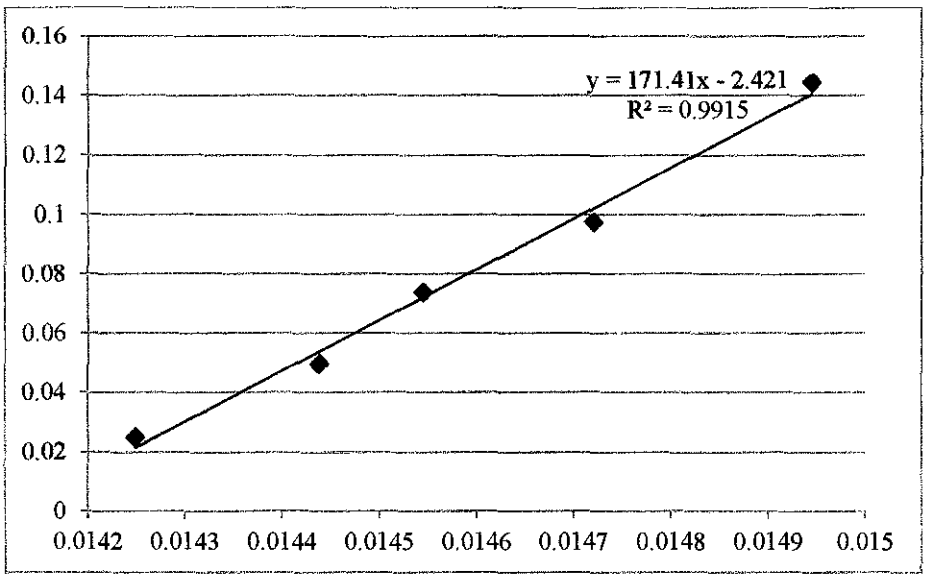


Figure 34: Langmuir Isotherm

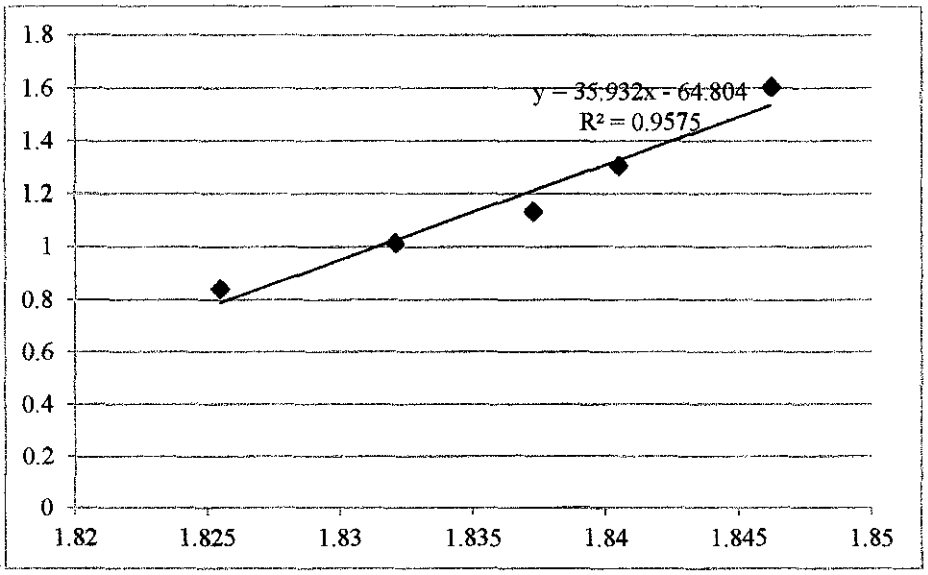


Figure 35: Freundlich Isotherm

Figure above shows the Langmuir and Freundlich isotherms plots of Pb(II) adsorption by rice husk based activated carbon. Figure 33 and 34 shows that both models seem to describe experimental data as the values of coefficient of determination are 0.9915 for Langmuir isotherm and 0.9575 for Freundlich isotherm. Both isotherms exhibit a very nice fit to adsorption data of Pb(II), however Langmuir isotherm model is slightly better compared to Freudlich isotherm.

CHAPTER 5: CONCLUSION & RECOMMENDATION

CONCLUSION

1) It can be expected that rice husk will show substantial potential as a cheaper alternative for activated carbon to remove Pb(II) ion from wastewater.
2) Chemical treatment with sodium hydroxide (NaOH) and carbonization allows for more pores development for rice husk producing highly porous rice husk based activated carbon with high adsorption capacity.
3) Adsorption of Pb(II) ion increases as contact time increases until it reaches equilibrium.

RECOMMENDATION

1) Other factors such as level of pH, particle size of adsorption and carbonization temperature should be further explored to properly determine the effects on the adsorption process.

2) Characterization using other equipment such as SEM is highly advisable since it provides better image quality with better details of the rice husk samples compared to FESEM.

3) For the treatment method, using other material than base such as acid like HCl is recommended to compare the pores development between rice husk treated with base and acid.

4) For future studies, it is also recommended to use different types of rice husk such as microwave incinerated rice husk ash to see the difference in absorptivity.

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APPENDICES

APPENDIX I

PROJECT TIMELINE

Timelines for FYP 1

No.	Activities /Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic	■	■												
2	Preliminary Research Work		■	■	■	■	■								
3	Submission of Extended Proposal							●							
4	Proposal Defence								■	■	■				
5	Project work continues											■	■		
6	Submission of Interim Draft Report													●	
7	Submission of Interim Report														●

Timelines for FYP 2

No.	Activities /Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project work continues	■	■	■	■	■	■	■							
2	Submission of progress report								●						
3	Project work continues								■	■	■	■	■		
4	Pre EDX											●			
5	Submission of Draft Report												●		
6	Submission of Dissertation (soft bound)													●	
7	Submission of Technical Paper													●	
8	Oral Presentation														●
9	Submission of Project Dissertation (Hard Bound)														●

■ Process ● Milestone

Figure 2: Gantt charts and key milestone

APPENDIX II

Calculation of 100 ppm of Pb(II) ion solution

To reduce errors, the solution was is prepared from 500 ppm $Pb(NO_3)_2$

$$500\ ppm\ by\ mass = 500\ mg \frac{Pb^{2+}}{1\ kg\ of\ water}$$

Provided the molar mass: Pb : 207.2g/mol

$Pb(NO_3)_2$: 331.2 g/mol

Assuming 1.0 mol of $Pb(NO_3)_2$, therefore having 1.0 mol of Pb^{2+}

$$Mass\ of\ Pb^{2+}\ ion = \frac{207.2\ g\ Pb^{2+}}{1\ mol\ of\ Pb^{2+}} \times 1\ mol\ of\ Pb^{2+}$$

$$= 207.2\ g\ Pb^{2+}$$

$$Mass\ of\ Pb(NO_3)_2\ ion = \frac{331.2\ g\ Pb(NO_3)_2}{1\ mol\ of\ Pb(NO_3)_2} \times 1\ mol\ of\ Pb^{2+}$$

$$= 331.2\ g\ Pb(NO_3)_2$$

$$Percent\ mass\ of\ of\ Pb^{2+}\ ion = \frac{207.2\ g\ Pb^{2+}}{331.2\ g\ Pb(NO_3)_2} = \frac{0.6256\ g\ Pb^{2+}}{1.000\ g\ Pb(NO_3)_2}$$

500 mg of Pb^{2+} in $Pb(NO_3)_2$:

$$500 \times 10^{-3} g\ of\ Pb^{2+} \times \frac{1.000\ g\ Pb(NO_3)_2}{0.6256\ g\ Pb^{2+}} = 0.799g$$

Using dilution formula, $M_1V_1 = M_2V_2$

$500\ V_1 = 150(1000\ ml)$

$V_1 = 300ml$

300 ml of 500 ppm of Pb(II) ion solution needs to be diluted to prepare 150 ppm of Pb^{2+}

APPENDIX III

Calculation for percent metal uptake

The calculation for metal uptake is listed below:

$$\frac{Initial\ concentration - Final\ Concentration}{Initial\ Concentation} \times 100\%$$

For example, the initial concentration is 150 ppm and the final concentration is 66.8 ppm, therefore the percent metal uptake would be:

$$\frac{150ppm - 66.8\,ppm}{150ppm} \times 100\% = \mathbf{55.46\%\ metal\ ion\ uptake}$$

Calculation for adsorption capacity

The calculation for adsorption capacity is listed below:

$$\frac{Volume\ of\ solution\ in\ liter(L) \times (Initial\ concentration - Final\ Concentration)}{Weight\ of\ rice\ husk\ in\ gram\ (g)}$$

For example, the initial concentration is 150 ppm and the final concentration is 66.8 ppm, volume of solution is 0.025 L and weight of rice husk used is 0.3g, the adsorption capacity would be:

$$\frac{0.025L \times (150ppm - 66.8ppm)}{0.03g}$$

$$= 6.93\ mg\ \frac{mg\ Pb(II)}{g\ rice\ husk}$$

APPENDIX IV

Figure 36. Raw rice husk

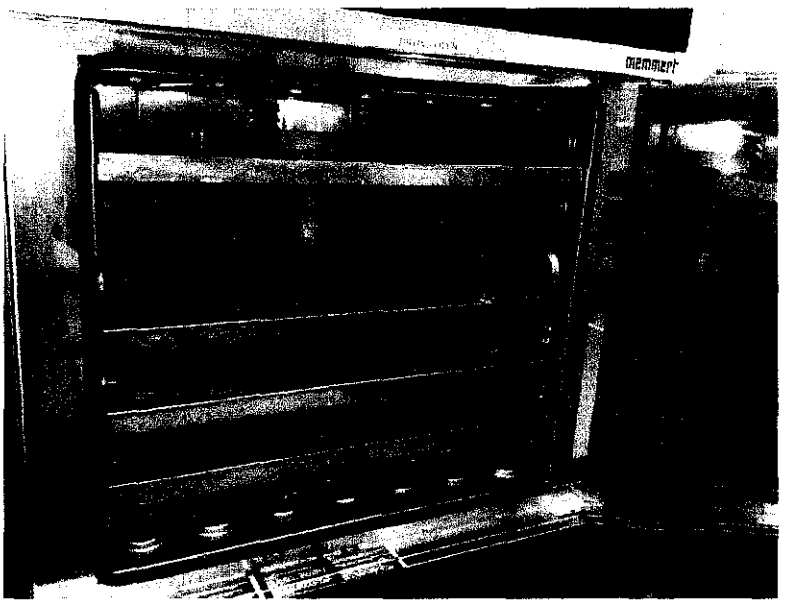

Figure 37. Oven used to dry rice husk sample

Figure 38. Electrical siever

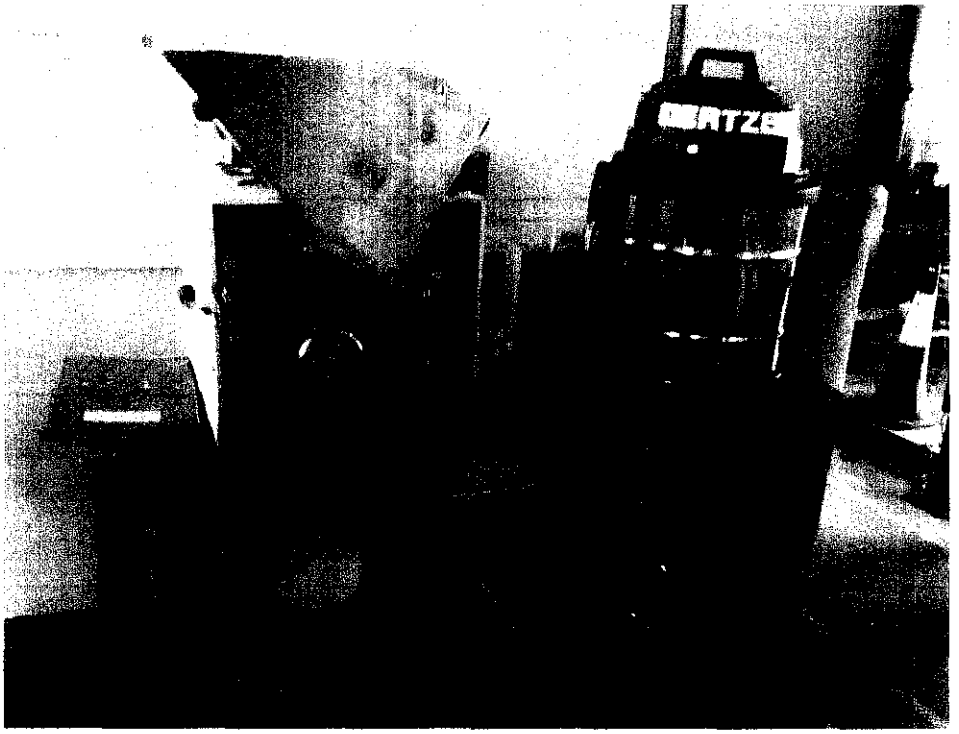

Figure 39. Grinder used for grinding rice husk

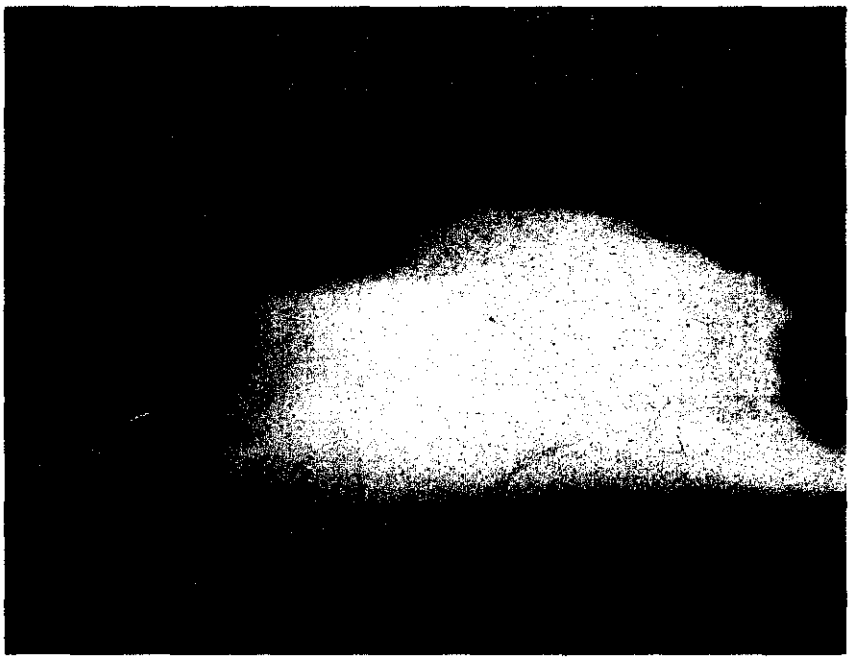

Figure 40. Grinded rice husk

Figure 41. Rice husk treated with 1.0M of sodium hydroxide(NaOH)

Figure 42. Furnace used for carbonization process

Figure 43. Carbonized rice husk

Figure 44. Adsorption study conducted using bath shaker